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We develope methodology for performing time dependent quantum mechanical calculations by representing the wave function as a sum of Gaussian wave packets (GWP), each characterized by a set of parameters such as width, position, momentum and phase. The problem of computing the time evolution of the wave function is thus reduced to that of finding the time evolution of the parameters in the Gaussians. This parameter motion is determined by minimizing the error made by replacing the exact wave function in the time dependent Schroedinger equation with its Gaussian representation approximant.

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This leads to first order differential equations for the time dependence of the parameters, and those describing the packet position and the momentum of each packet have some resemblance with the classical equations of motion. The paper studies numerically the strategy needed to achieve the best GWP representation of time dependent processes. The issues discussed are: the representation of the initial wave function; the numerical stability and the solution of the differential equations giving the evolution of the parameters; and the analysis of the final wave function. Extensive comparisons are made with an approximate method which assumes that the Gaussians are independent and their width is smaller than the length scale over which the potential changes. This approximation greatly simplifies the calculations and has the advantage of a greater resemblance to classical mechanics, thus being more intuitive. We find however that its range of applications is limited to problems involving localized degrees of freedom that participate in the dynamic process for a very short time. Finally we give particular attention to the notion that the GWP representation of the wave function reduces the dynamics of one quantum degree of freedom to that of a set of pseudo-particles (each represented by one packet) moving according to a "pseudo-classical" (i.e. classical like) mechanics whose "phase space" is described by a position and momentum as well as a complex phase and width.

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A STRATEGY FOR TIME DEPENDENT QUANTUM MECHANICAL CALCULATIONS USING A GAUSSIAN WAVE PACKET REPRESENTATION OF THE WAVE FUNCTION

by

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A Strategy For Time Dependent Quantum Mechanical Calculations Using A Gaussian Wave Packet Representation Of the Wave Function

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ABSTRACT

We develop methodology for performing time dependent quantum mechanical calculations by representing the wave function as a sum of Gaussian wave packets (GWP), each characterized by a set of parameters such as width, position, momentum and phase. The problem of computing the time evolution of the wave function is thus reduced to that of finding the time evolution of the parameters in the Gaussians. This parameter motion is determined by minimizing the error made by replacing the exact wave function in the time dependent Schroedinger equation with its Gaussian representation approximant. This leads to first order differential equations for the time dependence of the parameters, and those describing the packet position and the momentum of each packet have some resemblance with the classical equations of motion. The paper studies numerically the strategy needed to achieve the best GWP representation of time dependent processes. The issues discussed are: the representation of the initial wave function; the numerical stability and the solution of the differential equations giving the evolution of the parameters; and the analysis of the final wave function. Extensive comparisons are made with an approximate method which assumes that the Gaussians are independent and their width is smaller than the length scale over which the potential changes. This approximation greatly simplifies the calculations and has the advantage of a greater resemblance to classical mechanics, thus being more intuitive. We find however that its range of applications is limited to problems involving localized degrees of freedom that participate in the dynamic process for a very short time. Finally we give particular attention to the notion that the GWP representation of the wave function reduces the dynamics of one quantum degree of freedom to that of a set of pseudo-particles (each represented by one packet) moving according to a "pseudo-classical" (i.e. classical like) mechanics whose "phase space" is described by a position and momentum as well as a complex phase and width.

I. INTRODUCTION

In a series of papers Heller[1-10] developed a scheme for computing and interpreting time dependent quantum mechanical processes by representing the wave function as a superposition of Gaussian wave packets. Since each packet is characterized by several parameters, (the position and the momentum of the packet's center, a complex width and a complex phase) the calculation of the time evolution of the wave function is reduced to that of the time evolution of these parameters.

In his applied work Heller used a version of his method (which we call here the simplest Heller method (SHM) which is based on two simplifying assumptions. (1) The first assumes that if we must represent the wave function by a sum of Gaussians, we can propagate each Gaussian independently. This means that the equations of motion for the parameters of a Guassian G_A are not allowed to depend on the parameters of another Gaussian G_B. We call this the independent Gaussians approximation or IGA. (2) It is further assumed that throughout the (i.e., collision or photon absorption) process the width of each Gaussian is smaller than the length over which the potential changes. This allows the use, at each time step, of a second order Taylor expansion of the potential around the instantaneous center of the Gaussian. We call this the locally harmonic approximation (LHA).

SHM was used successfully by Heller to analyse a variety of time dependent processes such as atom-diatomic collision[1], photo-dissociation[7], photoabsorption[9], Raman scattering and atom diffraction by surfaces.[10] The method provides accurate results as well as a novel and beautiful interpretation of quantum dynamics in terms of a classical language. A common feature of these applications is that they all deal with the short time dynamics of localized quantum degrees of freedom; in a way their success reflects mostly Heller's skill in identifying important problems that fit the SHM validity conditions, rather than the

generality of the method.

The purpose of this paper is to explore the use the Gaussian wave packet (GWP) representation beyond the domain in which SHM is valid, by abandoning IGA and LHA. This is done in the spirit of Heller's work and requires mostly a revision of the manner in which his ideas are implemented.

For simplicity we consider one degree of freedom only (other cases will be discussed in future work) and assume that the wave function can be represented as a sum of Gaussians. This can always be done profitably if the degree of freedom is localized throughout the process of interest. The reduction of the propagation of the wave function to the propagation of the parameters describing the Gaussians is achieved by using what we call the minimum error method (MEM) (Section II); essentially this applies least square fitting type methods[11] to this particular problem and it contains a known "time dependent variational principle"[12] as a particular case. The latter was also used by Heller[12c] in the context of propagation of Gaussians.

The MEM equations, giving the time evolution of each Gaussian's parameters, give an accurate solution of the time dependent Schrodinger equation as long as the sum of Gaussians is a good representation of the wave function; that is, as long as the Gaussians provide an adequate basis set. In Section III we compare the MEM equations to those obtained by making the LHA and the IGA approximations (i.e. SHM). We show that MEM works very well in situations in which SHM has serious difficulties. Since one of the remarkable advantages of SHM is its ability of describing quantum processes in terms of classical concepts we pay special attention to the classical like physical picture underlying MEM, which we call here a pseudo-classical mechanics.

The remaining sections are concerned with more practical matters: the initial choice of the Gaussian representation (Section IV), the final state analysis (Section V) and the numerical stability of the MEM equations.

It is our feeling that the use of a Gaussian wave packet representation as implemented here, is likely to be very useful in treating quantitatively problems in which localized quantum degrees of freedom are involved in dynamic processes of moderately long duration. It is particularly suited to problems in which such degrees of freedom are coupled to a large number of classical variables whose state is specified only statistically (e.g. through a temperature) since the coupling of classical and quantum degrees of freedom presents, in this framework, no conceptual difficulty.

II. PROPAGATION

II.2 Mathematical Preliminaries

II.2.A. The minimum error method (MEM)

We are concerned with equations of the form

$$\dot{\psi} = A\psi \qquad \text{(II.1)}$$

where ψ is an unknown vector in a Hilbert space and A is a known time independent (this restriction is not necessary) operator. We assume that we know a physically motivated way of writing $\psi(t)$ in the form

$$\psi(x;t) \simeq \phi(x;\{\lambda_i(t)\}) \qquad \text{(II.2)}$$

where the explicit functional dependence of the approximant ϕ on the parameters $\lambda_1, \ldots, \lambda_N$ is known and the time dependence of ϕ takes place exclusively through $\lambda_1(t), \ldots, \lambda_N(t)$. Thus we can derive the time evolution of ψ by finding the parameter trajectories $\lambda_i(t)$ which satisfy

$$\partial\phi/\partial t = \frac{\partial\phi}{\partial\lambda_i}\dot{\lambda}_i = A\phi \ . \qquad \text{(II.3)}$$

(Repeated indices are summed over). Since we know the explicit dependence of ϕ, $A\phi$ and $\partial\phi/\partial\lambda_i$ on x and λ, we can use (II.3) to develop the following iteration scheme. We assume that $\lambda_i(t)$, $i = 1, \ldots, N$ are known and use (II.3) to compute $\dot{\lambda}_i$, $i=1, \ldots, N$; then we can determine $\lambda_i(t+\tau)$, for small τ, from

$$\lambda_i(t+\tau) = \lambda_i(t) + \dot{\lambda}_i\tau + 0(\tau^2) \ . \qquad \text{(II.4)}$$

and repeat the procedure. The scheme can be started at the initial time t=0 for which we know the wave function, therefore the values of $\lambda_i(0)$, $i = 1, \ldots, N$.

The equation (II.3) provides us with an infinite number of equations (one for each value of x) for the N unknowns $\dot{\lambda}_i(t)$. To deal with this situation we discretize the problem by using Eq. (II.3) at a finite number of points x_n, n=1, ..., M, M ≥ N. Thus, we have

$$(\partial\phi(x_n;\{\lambda\})/\partial\lambda_i)\dot{\lambda}_i = A\phi(x_n;\{\lambda\}) \qquad \text{(II.5)}$$

If we denote $C_{ni} = \partial\phi(x_n)/\partial\lambda_i$ and $B_n = A\phi(x_n)$ the matrix equation $C\dot{\lambda} = B$ is a set of M linear equations with N unknown and M ≥ N. Such equations appear in the "calculus of observations"[11] whenever the number of data points taken by overly industrious experimentalists exceeds by far the number of unknowns to be determined. A customary, but not unique, way to get the "best" solution is to minimize the quantity

$$\mathcal{E} = \sum_n W_n(C_{ni}\dot{\lambda}_i - B_n)^*(C_{nj}\dot{\lambda}_j - B_n) \qquad \text{(II.6a)}$$

with respect to the unknowns $\dot{\lambda}_i$. The weight W_n is included to allow us to de-emphasize the role played by the less reliable points n, or to enhance the influence of the reliable ones. The extremum (hopefully a minimum) conditions $\partial\mathcal{E}/\partial\dot{\lambda}_i=0$ (for simplicity we assume real parameters) lead to a N x N equation

$$\sum_j \left(\sum_n W_n\, C^+_{in}\, C_{nj}\right)\dot{\lambda}_j = B_i \qquad \text{(II.7a)}$$

where C^+ is the adjoint matrix of C and $C^+_{in} = C^*_{ni}$. This equation has a solution if the rank of the matrix $D_{ij}=\sum_n W_n C^+_{in} C_{nj}$ equals N. Since D is the Gram matrix of C the rank of D is equal to the rank of C. Thus, the parameters $\dot{\lambda}_i$ can be determined if the M x N matrix $C_{ni} = \partial\phi(x_n(\lambda))/\partial\lambda_i$ has one N x N minor whose determinant is non-zero. By taking the continuous limit (the x axis is divided in M segments of equal length Δx_n, x_n is taken in

the middle of the corresponding segment and $M \to \infty$) and using $W_n = \chi_n \Delta x_n$ we can rewrite (II.6) as

$$\mathcal{E} = \int dx \chi(x) \left(\frac{\partial \phi}{\partial \lambda_i} \dot{\lambda}_i - A\phi\right)^* \left(\frac{\partial \phi}{\partial \lambda_j} \dot{\lambda}_j - A\phi\right) \qquad \text{(II.6b)}$$

and (II.7) as

$$\int dx \chi(x) \left(\frac{\partial \phi}{\partial \lambda_i}\right)^* \left(\frac{\partial \phi}{\partial \lambda_j}\right) \dot{\lambda}_j = \int dx \chi(x) \left(\frac{\partial \phi}{\partial \lambda_i}\right)^* A\phi \quad . \qquad \text{(II.7b)}$$

This minimum error method (MEM) with the particular implementation given above reduces (when we take $\chi(x) = 1$) to the time dependent variational principle previously used in quantum mechanics.[12] The change of the point of view introduced by the above presentation has a "liberating" effect since: (a) it shows the tremendous richness and flexibility resulting from the existence of a large number of legitimate and resonable definitions for the "error" $\mathcal{E}$, each leading to different equations for the propagation of $\lambda_i(t)$; (b) it indicates that this is a mathematical procedure that can be applied to the propagation of any observable, not a physical principle tied to the wave function and the time dependent Schrodinger equation. Its main function is to reduce the propagation of $\psi(x,t)$ in the Hilbert space to the computation of N trajectories $\lambda_j(t)$ in R^N.

II.2.B. A Perturbation Theory Approach

The propagation scheme presented above seems to be of first order in the time step τ, since it solves Eq. (II.7b) for $\dot{\lambda}$ and then uses (II.4) to find $\lambda_i(t+\tau)$. We can attempt to use large time steps by considering that (II.7b) is a first order differential equation and by applying the Runge-Kutta (RK) method. However if Eq. (II.7b) is a first order expression in τ the use of a high order RK procedure would be incorrect, for the reasons explained below. Let us consider the equation $\dot{\lambda} = f(t) + O(\tau^2)$ and compare it to $\dot{\lambda} = f(t)$. The RK method applied to $\dot{\lambda} =$

f(t) uses the expansion

$$\lambda(t+\tau) = \lambda(t) + \dot{\lambda}(t)\tau + \ddot{\lambda}(t)\,\tau^2/2 + \dddot{\lambda}(t)\,\tau^3/3! + O(\tau^4). \tag{II.8a}$$

$$= \lambda(t) + f(t)\tau + \dot{f}(t)\tau^2/2 + \ddot{f}(t)\tau^3/3! + O(\tau^4) \tag{II.8b}$$

However if the equation is $\dot{\lambda} = f(t) + O(\tau^2)$ the expansion (II.8b) misses the third order term $\tau O(\tau^2)$ as well as the higher order terms originating from $\dot{O}(\tau^2)$ and $\ddot{O}(\tau^2)$.

To check whether the use of RK method to solve Eq. (II.7b) is legitimate we can compute (II.8a) by perturbation theory and compare it to the equation (II.8b) used by the RK method. We find that the two procedures coincide only when a certain definition of the error δ is used.

If we take a time step τ, causing a parameter change $\delta\lambda(t)$ equal to

$$\delta\lambda(t) = \dot{\lambda}(t)\tau + \ddot{\lambda}(t)\tau^2/2 + O(\tau^3) \tag{II.9}$$

the approximate wave function changes by

$$\delta\phi(t) = \phi(t+\tau) - \phi(\tau) = \frac{\partial\phi}{\partial\lambda}\left(\dot{\lambda}\tau + \ddot{\lambda}\,\frac{\tau^2}{2}\right) + \frac{1}{2}\,\frac{\partial^2\phi}{\partial\lambda^2}\left(\dot{\lambda}\tau+\frac{\ddot{\lambda}\tau^2}{2}\right)^2 - O(\tau^3) \tag{II.10}$$

The same change can be written as

$$\delta\phi(t) = A\phi(t)\tau + \frac{1}{2}\,A^2\phi(t)\tau^2 + O(\tau^3), \tag{II.11}$$

by expanding formally $\phi(t+\tau) = \exp\{A\tau\}\,\phi(t)$. Since the two expressions must coincide order by order we have

$$\frac{\partial\phi}{\partial\lambda_i}\,\dot{\lambda}_i = A\phi \tag{II.12a}$$

and

$$\frac{\partial\phi}{\partial\lambda}\,\ddot{\lambda} + \frac{\partial^2\phi}{\partial\lambda^2}\,\dot{\lambda}^2 = A^2\phi \qquad \text{(II.12b)}$$

This corresponds to using $\partial\phi/\partial t = A\phi$ and $\partial^2\phi/\partial t^2 = A^2\phi$ as two independent equations. We can now apply the minimum error method to them.

We have two infinite sets of equations to determine 2N unknowns $\dot{\lambda}_i$ and $\ddot{\lambda}_i$. Eq. (II.12a) is the same as (II.3) (thus giving the false impression that (II.3) is valid in first order only), but Eq. (II.12b) has not yet been used. To apply MEM to these two equations we define

$$\varepsilon_1 \equiv \int dx\chi(x)\left[\frac{\partial\phi}{\partial\lambda}\,\dot{\lambda} - A\phi\right]^*\left[\frac{\partial\phi}{\partial\lambda}\,\dot{\lambda} - A\phi\right] \qquad \text{(II.13)}$$

and use $\partial\varepsilon_1/\partial\lambda = 0$ to compute λ_i. This leads to Eq. (II.7b). Then we define

$$\varepsilon_2 \equiv \int dx\chi(x)\left[\frac{\partial\phi}{\partial\lambda}\,\ddot{\lambda} - \Phi(t)\right]^*\left[\frac{\partial\phi}{\partial\lambda}\,\ddot{\lambda} - \Phi(t)\right] \qquad \text{(II.14)}$$

with

$$\Phi(t) = A^2\phi - \frac{\partial^2\phi}{\partial\lambda^2}\,\dot{\lambda}^2 \qquad \text{(II.16)}$$

and use $\partial\varepsilon_2/\partial\ddot{\lambda} = 0$ to determine $\ddot{\lambda}$ ($\dot{\lambda}$ is already known by solving (II.7b)). This leads to

$$\int\chi(x)\,\frac{\partial\phi^*}{\partial\lambda}\,\frac{\partial\phi}{\partial\lambda}\,dx\,\ddot{\lambda} = \int dx\chi(x)\,\frac{\partial\phi^*}{\partial\lambda}\,\Phi(x;t)\ . \qquad \text{(II.17)}$$

Note that we could have legitimately defined the error as $\varepsilon = \varepsilon_1 + \varepsilon_2$ and used $\partial\varepsilon/\partial\dot{\lambda} = 0$ and $\partial\varepsilon/\partial\ddot{\lambda} = 0$ to generate equations for $\dot{\lambda}$ and $\ddot{\lambda}$. The equations obtained in this way are different from (II.7b) and (II.17). In particular, they do not give for $\ddot{\lambda}$ the same value as the time derivative of Eq. (II.7b).

We can now turn to our original question: Is $\ddot{\lambda}$ computed by taking derivatives of Eq. (II.7b) identical to the value of $\ddot{\lambda}$ given by Eq. (II.17)? A straightforward calculation shows that this is the case. Therefore a n-th order RK procedure applied to the first order "variational" equation (II.3) is equivalent to the use of a n-th order perturbation theory within MEM and is thus wholly justified. This is a pleasant result since the use of the existing RK programs, which compute the needed derivatives internally, can save a large amount of labor. Note, however, that the use of the error $\mathcal{E} = \mathcal{E}_1 + \mathcal{E}_2$ with the equations $\partial\mathcal{E}/\partial\dot{\lambda} = 0$ and $\partial\mathcal{E}/\partial\ddot{\lambda} = 0$ leads to equations for $\dot{\lambda}$ and $\ddot{\lambda}$ which are not equivalent to the RK expansion of Eq. (II.7b). This is true for other error definitions that we have considered.

II.2.C A Global Minimum Error Method

The applications of MEM discussed so far were all made by using errors defined locally in time. Below we discuss an extension of the method which has a truly variational character since it determines the trajectories $\lambda_i(t)$ which minimizes the error functional

$$\mathcal{E} = \int_0^T dt\, n(t) \int dx\, \chi(x) \left\{\frac{\partial\phi}{\partial\lambda_i}\dot{\lambda}_i - A\phi\right\}^* \left[\frac{\partial\phi}{\partial\lambda_j}\dot{\lambda}_j - A\phi\right] . \qquad \text{(II.18)}$$

The local method varies the numerical value of $\dot{\lambda}_i(t)$ so that the error $\mathcal{E}(t)$ made <u>at time</u> t, is minimized. In (II.18) the <u>whole curve</u> $\lambda_i(t)$ is adjusted to give a minimum value to $\mathcal{E}$. The weight $n(t)$ has been incorporated to permit us to emphasize or deemphasize, as desired, the importance of some of the points on the trajectory. Taking the functional derivative $\partial\mathcal{E}/\partial\lambda_i(t')$ and equating it to zero leads to

$$n(t)\mathrm{Re}\langle \partial\phi/\partial\lambda_\mu | ((\partial\phi/\partial\lambda_j)\dot{\lambda}_j - A\phi)\rangle [\delta(t-T)-\delta(t)]$$

$$-2(dn/dt)\mathrm{Re}\langle (\partial\phi/\partial\lambda_\mu) | ((\partial\phi/\partial\lambda_j)\dot{\lambda}_j - A\phi)\rangle$$

$$-2n(t)\mathrm{Re}\langle (\partial\phi/\partial\lambda_\mu) | [(\partial^2\phi/\partial\lambda_i\partial\lambda_j)\dot{\lambda}_i\dot{\lambda}_j + \frac{\partial\phi}{\partial\lambda_i}\ddot{\lambda}_i - A\frac{\partial\phi}{\partial\lambda_j}\dot{\lambda}_j\ ]\rangle$$

$$-2n(t)\mathrm{Re}\langle A\partial\phi/\partial\lambda_\mu | [(\partial\phi/\partial\lambda_j)\dot{\lambda}_j - A\phi]\rangle = 0 \qquad \text{(II.19)}$$

The first term appears because we have not specified any constraints for the variations $\delta\lambda_i(T)$ and $\delta\lambda_i(0)$ at the ends of the trajectory. We can eliminate it by taking $n(T) = n(0) = 0$. The second term is zero if $n(t)$ is a constant; if the first two terms are thus eliminated $n(t)$ disappears from the equation.

The equation obtained above is rather different from the preceeding ones and there are no theoretical grounds for rejecting one in favor of the other. The existence of so many ways of generating the trajectories in the parameter space originates from the fact the the "best" solution of an infinite set of equations having a finite number of unknowns is not uniquely defined.

II.3 PHYSICAL APPLICATIONS OF MEM

II.3.A The propagation of the wave function.

In the application presented below MEM is identical to a known "variational principle".[3,12] Its application to the propagation of Gaussian wave functions has been briefly discussed by Heller.[3d] Therefore we present it here with a minimum of details which are indispensable for understanding what follows.

We consider a representation of the wave function of the form

$$\psi(x;t) = \sum_{A=1}^{N_G} G_A(x;\{\Lambda_{A\alpha}\};\{\Gamma_{Aa}\}) \qquad \text{(II.21)}$$

where the parameters $\Lambda_{A\alpha}(t)$, $\alpha = 1,2, \ldots, C_A$ are complex functions of time and $\Gamma_{Aa}(t)$, $a=1, 2, \ldots, R_A$ are real functions of time, and C_A and R_A are integers. The equation (II.21) represents the wave function $\psi(x;t)$ as a sum of localized "fragments" G_A whose explicit dependence on the parameters Λ and Γ is known. For a variety of reasons, well summarized in Heller's papers,[1-10] the use of complex Gaussians for G_A is particularly advantageous. Other functions of the form

$$(\sum_{n=0}^{m} Q_n(t)(x-\beta_n(t))^n)G_A(x;\{\Lambda_{A\alpha}\},\{\Gamma_{Aa}\})$$

where $Q_n(t)$ and $\beta_n(t)$ are functions whose time dependence is to be determined and G_A is a complex Gaussian, have similar advantages and greater flexibility.

To calculate the parameter trajectories (i.e. the time dependence of $\Lambda_{A\alpha}$ and Γ_{Aa}) we use MEM with the definition (II.6b) for the error δ and the operator $A = (i\hbar)^{-1}H$, where H is the Hamiltonian.

The use of the weighting function $\chi(x)$ require some comment since previous applications of the "variational principle" use $\chi(x)=1$. In most dynamic problems we are not interested in computing the wave function, but its projection on some given, time independent state $|\tau(0)>$. For example in computing the total absorption cross section for an electronic excitation of a molecule by light we must propagate in time the nuclear wave function $\tau(x;0) \equiv <x|\tau(0)>$ of the electronic ground state on the final electronic energy surface (Franck-Condon approximation is implied), to obtain the wave function $\tau(x;t) \equiv <x|\tau(t)>$; the Fourier transform of $<\tau(t)|\tau(0)>$ with respect to t gives the total absorption cross section. One can show in fact that such quantities are generalizations of the one particle Green's functions used in many body theory from the case of a quasi-particle excitation to that of a transition from one many-body state to another. If our intent is to compute such overlaps we might as well weight the error $\mathcal{E}$ accordingly by taking $\chi(x) = \tau(x;0)^{*}\tau(x;0)$. Thus we determine $\Lambda_{A\alpha}$ and Γ_{Aa} so that the wave function $\psi(x;t)$, given by Eq. (II.21), has minimum error for those values of x where $\chi(x)$, hence $\tau(x;0)$ is not zero. If $\tau(x;0)$ is very localized this procedure should allow us to fit $\psi(x;t)$ with fewer fragments $G_A(x;\{\Lambda\},\{\Gamma\})$ than in the case when we try to fit the wave function in the whole space.

Applying MEM to the approximant defined by (II.21) and the error defined by (II.6b) gives

$$\mathcal{E} \equiv A_{A\mu;A'\mu'}\dot{\Lambda}^{*}_{A\mu}\dot{\Lambda}_{A'\mu'} + C_{Aa;A'a'}\dot{\Gamma}_{Aa}\dot{\Gamma}_{A'a'} - B_{A\mu;A'a'}\dot{\Lambda}^{*}_{A\mu}\dot{\Gamma}_{A'a'} + B^{*}_{A\mu;A'\mu'}\dot{\Lambda}_{A\mu}\dot{\Gamma}_{A'a'} + D_{A\mu}\dot{\Lambda}^{*}_{A\mu} + D^{*}_{A\mu}\dot{\Lambda}_{A\mu} + E_{Aa}\dot{\Gamma}_{Aa} + E^{*}_{Aa}\dot{\Gamma}_{Aa} \qquad (II.22)$$

with

$$A_{A\mu;A'\mu'} = \hbar^2 \langle (\partial G_A/\partial \Lambda_{A\mu}) | (\partial G_{A'}/\partial \Lambda_{A'\mu'}) \rangle \ , \qquad \text{(II.23a)}$$

$$B_{A\mu;A'a'} = \hbar^2 \langle (\partial G_A/\partial \Lambda_{A\mu}) | (\partial G_{A'}/\partial \Gamma_{A'a'}) \rangle \ , \qquad \text{(II.23b)}$$

$$C_{Aa;A'a'} = \hbar^2 \langle (\partial G_A/\partial \Gamma_{Aa}) | (\partial G_{A'}/\partial \Gamma_{A'a'}) \rangle \ , \qquad \text{(II.23c)}$$

$$D_{A\mu} = i\hbar \langle (\partial G_A/\partial \Lambda_{A\mu}) | H\psi \rangle \ , \qquad \text{(II.23d)}$$

$$E_{Aa} = i\hbar \langle \partial G_A/\partial \Gamma_{Aa}) | H\psi \rangle \ . \qquad \text{(II.23e)}$$

and

$$\langle \phi(x) | \psi(x) \rangle \equiv \int dx \ \chi(x) \phi^*(x) \psi(x) \qquad \text{(II.24)}$$

To minimize $\mathcal{E}$ with respect to the complex parameters, as required by MEM, we can use $\dot{\Lambda}^*_{A\mu}$ as independent variables and generate one complex equation (for $\dot{\Lambda}_{A\alpha}$ and $\dot{\Gamma}_{Aa}$) from each condition $\partial\mathcal{E}/\partial\dot{\Lambda}^*_{A\mu} = 0$. The condition $\partial\mathcal{E}/\dot{\Gamma}_{Aa} = 0$ for the real unknown $\dot{\Gamma}_{Aa}$ leads to one real equation. These equations are

$$A_{B\beta;A\mu}\,\dot{\Lambda}_{A\mu} + B_{B\beta;Aa}\dot{\Gamma}_{Aa} + D_{B\beta} = 0 \qquad \text{(II.25a)}$$

and

$$(\mathrm{Re}C_{Bb;Aa})\,\dot{\Gamma}_{Aa} + \mathrm{Re}(B_{A\mu;Bb}\dot{\Lambda}^*_{A\mu}) + \mathrm{Re}\ E_{Bb} = 0 \qquad \text{(II.25b)}$$

Previous work treated all parameters as if they were complex thus generating one unneeded equation for each real parameter. In all the cases that we are aware of this does not lead to errors or serious complications since the superfluous equations can be eliminated by inspection; they are linear combinations of the other equations. For more complicated representations of $\psi(x;t)$ it is easier to use the procedure described here, which gives only the necessary equations, thus avoiding the extra work needed to carry out the elimination mentioned above.

II.3.B The propagation of various observables

Since the wave function contains all the information we can possibly want to know about the system, it contains superfluous information whenever we are interested in a small number of observables. Assuming that there is some proportionality between the amount of information wanted and the effort required to get it[13] we might hope to save labor by determining the parameter trajectories that give the best fit to the observables of interest only, rather than by fitting the whole wave function. In the case already mentioned, when we want the overlap of $\psi(x;t)$ with a localized function $\tau(x;0)$, we can hope to need fewer "pieces" G_A (e.g. Gaussians) if we determine $\psi(x;t)$ only in the spatial region where $\tau(x;0)$ is large. Similarly, if the variation of the wave function $\psi(x;t)$ with x, at a fixed post-collision value of t, has a broad hump on a length scale L with small wiggles on the scale l superimposed on it, then a matrix element with a planar wave function of momentum of order $\hbar 2\pi/l$ is totally indifferent to the existence of the hump; it is however very sensitive to the details of the wiggles. Therefore a calculation that gets the wiggles right and misses the hump is quite satisfactory. Again, one can hope that such diminished demands on the quality of the wave function requires less work (i.e. fewer Gaussians) than the case when we attempt to fit $\psi(x;t)$ with wiggles, humps and whatever else.

Since MEM is a method of solving differential equations, rather than a variational principle specifically tied to $i\hbar\partial\psi/\partial t = H\psi$, we can apply it to generate parameter trajectories that give adequate results for some observable. Several examples, which should provide ample illustration on how to proceed in general, are given below. For simplicity we confine ourselves to the case of one approximant (rather than a sum, as in Eq. (II.21)) and several real parameters λ_i. The generalization to

the case (II.21) is straightforward.

(α) The use of the transition probability to determine the parameter trajectories.

Let us assume that at post-collision times we are interested in the probability that the systems described by $\psi(t)$ is in a continuum state $|k\rangle$. Taking the time derivative of the probability

$$P(k;t) \equiv |\langle k|\psi(t)\rangle|^2 , \qquad (II.26)$$

using Eq. (II.2) to approximate $\psi(t)$, and the Schrodinger equation to compute $\dot{\phi}$, we obtain

$$\dot{P}(k;t) = (\partial P/\partial\lambda_i)\dot{\lambda}_i = (2/\hbar)\ \mathrm{Im}\ \langle k|H\phi\rangle\langle\phi|k\rangle \equiv f(k;t) \qquad (II.27)$$

Since this must be satisfied for all values of k (spanning the continuum) we have again an infinite number of equations and N unknowns $\dot{\lambda}_i$. MEM determines the unknowns by generating an NxN equation for them. This is obtained by minimizing

$$\mathcal{E} = \int dk\ \chi(k)\ \{(\partial P/\partial\lambda_i)\dot{\lambda}_i - f(k;t)\}^2 \qquad (II.28)$$

with respect to $\dot{\lambda}_i$. The result is

$$(\int dk\ \chi(k)\ \frac{\partial P}{\partial\lambda_i}\ \frac{\partial P}{\partial\lambda_j})\dot{\lambda}_j = \int dk\chi(k)(\frac{\partial P}{\partial\lambda_i})\ f(k;t)\ . \qquad (II.29)$$

Since we know the functional dependence of ϕ on $\lambda_i(t)$ we can compute the matrix elements appearing in (II.29) whenever we know the values of all the λ_i at t. This allows us to determine $\dot{\lambda}_i(t)$ and $\lambda_i(t+\tau)\cong\lambda_i(t)+\dot{\lambda}_i(t)\tau$, providing us with an iteration scheme to get $\lambda_i(t)$ at all subsequent times. If ϕ is a Gaussian and $|k\rangle$ a planar wave then $\langle\phi|k\rangle$ is a Gaussian and $\langle k|H\phi\rangle$

contains moments of a Guassian (from the kinetic energy operator) and integrals of the form $\int dx\ \exp(-ikx)(x-x_t)^n V(x)\phi(x)$. The latter can be performed analytically if $V(x)$ is fitted by Gaussians, exponentials, polynomials or any combination of them.

The same procedure can be applied when we are interested in $P_n(t) = |\langle n|\psi(t)\rangle|^2$, where n is a discrete state. The equation of motion is

$$(\partial P_n/\partial\lambda_i)\dot{\lambda}_i = (2/\hbar)\ \mathrm{Im}\langle n|H\phi\rangle\langle\phi|n\rangle \equiv f_n(t) \qquad \text{(II.30)}$$

If the number of wave functions $|n\rangle$ used in Equation (II.30) is larger than the number of unknowns $\dot{\lambda}_i$ (this is always the case in a Hilbert space of infinite dimension) then MEM gives

$$\left[\sum_n \varkappa_n(\partial P_n/\partial\lambda_i)(\partial P_n/\partial\lambda_j)\right]\dot{\lambda}_j = \sum_n \varkappa_n \frac{\partial P_n}{\partial\lambda_i} f_n(t)\ , \qquad \text{(II.31)}$$

where $\varkappa_n$ is a weighting factor.

Note that the projection on discrete basis sets to give the probability P_n is of interest in bound state dynamical problems (e.g. a semi-classical external field drives the system into a steady state which is a superposition of the eigenstates of the system). In collision theory we need probabilities of the form $|\langle k|\langle n|\psi(t)\rangle|^2 \equiv P_{n,k}(t)$ in which k describes the relative translational motion and n the internal states of the fragments. MEM can be applied to such situations (to compute trajectories determined for the best fit of these probabiliites) with no additional conceptual difficulty.

(β) The use of expectation values to determine the trajectories.

If we are interested in knowing the expectation value of an operator O at time t we can use it to generate trajectory

equations. We have

$$\frac{d}{dt}\langle\phi(t)|O|\phi(t)\rangle = \sum_n O_{nn}\frac{dP_n(t)}{dt} = \sum_n O_{nn} f_n(t) \qquad (II.32)$$

where P_n is defined by (II.26) and f_n by (II.27) (we assume here that the discrete basis set provided by the eigenvectors of O can describe adequately the dynamics, thus only $O_{nn} = \langle n|O|n\rangle$ appears). We can now use the error

$$\mathcal{E} = \sum_n (O_{nn})^2\{(\partial P_n/\partial\lambda_i)\dot{\lambda}_i - f_n(t)\}^2 \qquad (II.33)$$

in which the probability equations (II.30) are weighted by the matrix elements of the operator O. Thus the importance of the states likely to contribute more to the mean value of O is emphasized and the others are weighted down or multiplied by zero. By equating with zero derivatives of $\mathcal{E}$ with $\dot{\lambda}_i$ we obtain (II.31) with the weight $\alpha_n \equiv \langle n|O|n\rangle$.

III. Approximate Propagation Schemes

III.1 Introductory Remarks

The equations (II.25) can in principle be used to find the time evolution of the wave function by finding the parameter trajectories. If the physics of the problem forces us to use too many Gaussians we might have to abandon the method or to look for some simplified propagation schemes.

To see how rapidly the complexity of the method can escalate let us consider a time dependent quantum mechanical problem involving two three-dimensional variables $\vec{R}$ and $\vec{r}$. We need nine complex parameters for the width matrix for the variable $\vec{R}$ and nine for $\vec{r}$; we must also use terms of the form $(\vec{R}-\vec{R}_t)\cdot\overleftrightarrow{C}\cdot(\vec{r}-\vec{r}_t)$ to permit correlations between the two degrees of freedom and this requires nine complex parameters. Thus the characterization of the width of the Gaussian requires 27 complex parameters. To this we must add 6 positions, 6 momenta and a complex phase. Thus if we deal with six correlated degrees of freedom we need a total of 68 real parameters per Gaussian. For ten Gaussians we must solve 680 first order differential equations.

Assuming that in the dumbest possible way we saturate the space with Gaussians and are willing to solve 700 (or even 7000) equations, the method could still be used since all the labor required to carry out the integration to obtain the parameter trajectories is thus roughly comparable to that needed in molecular dynamics; seven thousand equations corresponds there to 2333 atoms, which is fully within the capability of present day computers.

The disadvantage of such a brute force attack is the loss of the simplicity which makes the Heller method so appealing in the first place. It is not surprising therefore that most of

Heller's effort was directed towards simplfying the parameter equations of motion. Such simplifications are physically motivated and their success depends on the problem being addressed. Nevertheless some of their features are such that can be discussed in a general setting.

All numerical calculations carried out so far have used two approximations. (1) If the wave function was constructed as a sum of Gaussians, it was assumed that matrices $A_{B\beta;A\mu}$, $B_{B\beta;Aa}$, $ReC_{Bb;Aa}$ and $D_{A\mu;Bb}$ are diagonal in the indeces B and A which label different Gaussians. This approximation decouples the Gaussians and we call it here the independent Gaussian approximation (IGA). (2) If we assume that each independent Gaussian is, throughout the collision, narrower than the spatial range over which the potential changes appreciably, we can further simplify the matrix elements since they can be evaluated by expanding the potential in power series around the center of the Gaussian and by retaining the first three terms of the expansion. That is, at time t we use

$$V(\vec{r}) \simeq V(\vec{r}_t)+(\partial V(\vec{r}_t)/\partial \vec{r}_t)(\vec{r}-\vec{r}_t)+(1/2)\partial^2 V(\vec{r}_t)/\partial \vec{r}_t^{\,2}\ (\vec{r}-\vec{r}_t)^2$$

where $\vec{r}_t$ is the center of the Gaussian. In what follows we call this the local harmonic approximation (LHA). The main appeal of this approximation is that the mean position (i.e. the center of the packet) and the mean momentum of packet move according to classical mechanics. As shown by Ehrenfest[14] this property has nothing to do with the use of Gaussians for $G_A(\vec{r},\{\lambda_A\})$; it is valid whenever the region over which G_A is non-zero is smaller than the spatial range over which the potential changes. A further appealing feature of LHA is the fact that the phase γ_t is essentially the classical action along the trajectory followed by the center of the packet, which is in agreement with the eikonal approximation.

The theory resulting after making these two approximations is called in what follows the simple Heller method (SHM). It has been successfully applied to a number of problems chosen so that the risk of SHM break-down was minimized. A beautiful example is the absorption coefficient of a photodissociating molecule. The initial state is bound and very localized. The absorption cross section is given (essentially) by the Fourier transform with respect to time of the overlap between the initial wave function and the time dependent wave function obtained by propagating the initial wave function on the upper state. If the fragments produced by photo-dissociation separate very quickly (i.e. they are on a strongly repulsive potential) the overlap becomes zero very quickly. Therefore they need to propagate a very localized packet for a very short time; it is not likely that it will have time to broaden to the extent that will cause LHA to give substantial errors. By using SHM Heller has developed a beautifully clear and simple picture of the connection between the absorption spectrum and the classical motion on the upper state on which the dissociation takes place. That stimulated equally elegant experiments.[15] Other successful calculations involved harmonic oscillators for which - as we show later - SHM is exact.

Recent calculations by Skodje and Truhlar[16] and by Heather, Jackson and Metiu[17] show, however, that the method fails to give correct values for the time evolution of the states of the Morse oscillator. We are thus led to examine both theoretically and numerically the two approximations mentioned above. Our conclusion is that they are justified only under special circumstances.

III.2 The Local Harmonic Approximation (LHA)

III.2.A The definition of the approximation

We consider here the case of one normalized Gaussian, to isolate the effects of LHA from those of the neglect of the interaction between Gaussians. Using the equations (A.3) - (A.7) of Appendix A we can write the MEM equation for the case of the Gaussian approximant

$$\psi(x;t) \simeq G(x) = \exp\{(i/\hbar)[\alpha(x-R)^2 + P(x-R) + \gamma]\} \qquad \text{(III.1a)}$$

as

$$M_4(\dot{\alpha}+2\alpha^2/m) + M_2[\dot{\gamma}-P\dot{R}-i\hbar\alpha/m + P^2/2m] + V_2=0 \ , \qquad \text{(III.1b)}$$

$$M_2(\dot{\alpha}+2\alpha^2/m) + [\dot{\gamma}-P\dot{R}-i\hbar\alpha/m + P^2/2m] + V_o=0 \ , \qquad \text{(III.1c)}$$

$$\mathrm{Re}\Omega = 0 \ , \qquad \text{(III.1d)}$$

$$\mathrm{Im}\Omega = 0 \ , \qquad \text{(III.1e)}$$

with

$$\Omega = M_2[2\alpha(P/m-\dot{R}) + \dot{P}] + V_1 = 0 \ , \qquad \text{(III.2)}$$

$$M_n = \langle (x-R)^n \, G|G\rangle \ , \qquad \text{(III.3)}$$

and

$$V_n = \langle (x-R)^n G|VG\rangle \ . \qquad \text{(III.4)}$$

The equation (III.1e) leads to

$$\dot{R} = P/m \ , \qquad \text{(III.5a)}$$

and this together with (III.1d) gives

$$\dot{P} = -V_1/M_2 = -\frac{\partial}{\partial R}\frac{\langle G|V|G\rangle}{\langle G|G\rangle} = -\frac{\langle G|(\partial V/\partial x)|G\rangle}{\langle G|G\rangle} \ . \qquad \text{(III.5b)}$$

The equations (III.5) are more general than the procedure used here for their derivation. Since R and P are the

expectation values of the position and momentum operators for a Guassian state the equations (III.5) also follow from Ehrenfest's theorem.[14]

Combining (III.1b) and (III.1c) we can write:

$$[\dot{\gamma}-P\dot{R}-i\hbar(\alpha/m) + P^2/2m] = -(M_4V_o-M_2V_2)/(M_4-M_2^2) \qquad \text{(III.5c)}$$

and

$$\dot{\alpha}+2\alpha^2/m = (M_2V_o-V_2)/(M_4-M_2^2) \ . \qquad \text{(III.5d)}$$

The LHA assumes that at any time t we can replace the potential by

$$V(x) \simeq V(R) + (\partial V(R)/\partial R)(x-R(t)) + (1/2)(\partial^2 V(R)/\partial R^2)(x-R(t))^2 \ . \qquad \text{(III.6)}$$

Using this expression for V(x) in the equations (III.5) leads to the LHA equations:

$$\dot{R} = P/m, \qquad \text{(III.7a)}$$

$$\dot{P} = -\partial V(R)/\partial R \ , \qquad \text{(III.7b)}$$

$$\dot{\gamma} - P\dot{R} - i\hbar\alpha/m + P^2/2m + V(R) = 0 \ , \qquad \text{(III.7c)}$$

$$\dot{\alpha} +2\alpha^2/m = -(1/2)\partial^2 V(R)/\partial R^2 \ . \qquad \text{(III.7d)}$$

In what follows we attempt to establish the limitations of the LHA equations (III.7) by comparing them to the MEM equations (III.5) from a physical and a numerical point of view.

III.2.B <u>The magnitude of the error made by LHA.</u>

Clearly the expansion (III.6) is valid only if V(x) is

practically constant as x varies around R over a spatial range equal to the width of the Gaussian. A more precise statement can be made by retaining the next terms in the potential expansion and requiring that they should contribute less than 10% to the equation of motion. Adding a third order term to Eq. (III.6) and using it in Eq. (III.5b) we obtain

$$(\dot{P}_{MEM} - \dot{P}_{LHA})/\dot{P}_{LHA} = [l(t)^2/4][\partial^3 V(R(t))/\partial R(t)^3][\partial V(R(t))/\partial R(t)]^{-1} + O(l^4) \qquad \text{(III.8)}$$

Here $\dot{P}_{LHA}$ is given by Eq. (III.7b) and $\dot{P}_{MEM}$ is the MEM value of $\dot{P}$ when the third order term is included in the potential expansion. The length $l(t) = [\hbar/2Im\alpha(t)]^{1/2}$ is the width of the Gaussian. The error made by using $\dot{P}_{LHA}$ instead of $\dot{P}_{MEM}$ is less than 10% if

$$(l^2/4)(\partial^3 V/\partial R^3)/(\partial V/\partial R) \leq 0.1 \qquad \text{(III.9)}$$

We have found, by a similar analysis, that the errors in the other LHA equations are smaller than 10% if (III.9) is satisfied. In other words, the LHA equation (III.7b) is the one giving the largest error.

For an exponential potential $V(x) = e^{-\lambda x}$ Eq. (III.9) gives

$$l^2\lambda^2 \leq 0.4 \qquad \text{(III.10)}$$

and for a repulsive Lennard-Jones potential

$$l^2\ 13\cdot 14/R_T^2 \leq 0.4\ , \qquad \text{(III.11)}$$

where R_T is the value of R at the turning point (where we expect LHA to have more difficulties). For a kinetic energy of 0.05 eV (thermal for He), $\sigma = 4$Å, $\epsilon/k \simeq 54^oK$ and $V(x) = 4\epsilon[(\sigma/x)^{12} - (\sigma/x)^6]$ we find (from (III.11)) that LHA is satisfactory (within 10%) if $l \leq 0.08$ Å. Roughly the same result is obtained from

(III.10) for $\lambda^{-1} \simeq 0.2\text{Å}$ (a rapidly varying "hard wall" potential). Less stringent conditions are required in the smoother regions of the potentials.

In our calculations of scattering of He from solid surfaces[18] we find that l exceeds this value in all cases, even though we have varied the initial width (both Re α and Im α) in an attempt to obtain narrow packets in the interaction region.

To get a better understanding of the breakdown of LHA we carried out several calculations in which the Gaussian wave packet (GWP) (III.1a) is propagated in the Morse potential

$$V(x) = D\{1+\exp[-2\lambda(x-x_o)] - 2\exp[-\lambda(x-x_o)]\} . \qquad \text{(III.12a)}$$

In Fig. 1 we plot l(t) as a function of time, for a normalized, initially narrow low energy wave packet. Since the Morse potential is the sum of two exponentials (one of which has the length scale $(2\lambda)^{-1}$) the validity condition for LHA is given by Eq. (III.10) (with λ replaced by 2λ). This leads to $l\lambda = 0.31$. We expect LHA to work best either for a low energy GWP, which samples the lower part of the potential which is nearly harmonic, or for packets which are initially sufficiently narrow. We see that more than half of the time $\lambda l(t)$ is above $l\lambda = 0.31$, indicating that the conditions for the validity of LHA are not fulfilled.

It is important to realize that in order to be a useful approximation LHA must be uniformly accurate; that is, if $f_e(t)$ and $f_a(t)$ are the exact and the approximate values of a parameter we must have $\int|f_e(t)-f_a(t)|dt<\epsilon_1$ as well as max $|f_e(t)-f_a(t)|<\epsilon_2$ for $t\in[0,T]$. Here T is the time interval over which we need to know the evolution of the packet, and ϵ_1 and ϵ_2 are small numbers specifying the error we are willing to tolerate. The reason for this can be understood by considering

the trajectory of the center of the packet. Let us assume that LHA gives us the incorrect force only for $t \in [t_1, t_1+\Delta]$. This will distort the trajectory for the remainder of the time, even though the force is computed correctly at all $t \geq t_1 + \Delta$, because the values of $R(t_1+\Delta)$ and $P(t_1+\Delta)$ are erroneous, and therefore the trajectory will stray from the correct path at $t > t_1 + \Delta$.

A more precise test of LHA's accuracy is made in Fig. 2 where we plot $- V_1/M_2$ and $- \partial V(R(t))/\partial R(t)$, which are the right hand sides of the MEM and LHA equations (III.5b) and (III.7b), respectively, giving the evolution of the mean momentum. Thus we are comparing the expectation value of the operator $- \partial V/\partial x$ to the classical force; if LHA works these two quantities must be equal. Again, we see that this is not the case.

In evaluating the LHA accuracy we must keep in mind that the trajectories of R and P are not measurable in a quantum experiment. Normally we measure the projection of the asymptotic wave function on a set of final states. It is conceivable that such projections are not very sensitive to errors in trajectories and LHA might be better than an analysis of the trajectory might suggest. On the other hand these trajectories are used to give a qualitative description of the dynamic process in a language that is close to classical mechanics; large errors in the trajectory would lead to a misleading qualitative representation of dynamics.

III.2.C A comparison between the pseudo-classical mechanics generated by MEM and the classical mechanics (given by LHA).

The MEM Equations (III.5a-b) have some resemblance to the classical equations of motion for the coordinate and momentum; when LHA is used they reduce to Hamilton's equations with the classical potential V(R(t)). To emphasize both the fact that the MEM equations (III 5.a-b) are quantum equations for the

expectation values of the position and momentum operator in a Gaussian state and the fact that they resemble classical equations, we call them pseudo-classical equations; and we use the term pseudo-classical mechanics for the motion of R(t) and P(t) generated by them. For a single Guassian the difference between MEM and LHA is thus equivalent (as far as R(t) and P(t) are concerned) to the difference between the pseudo-classical and the classical mechanics. Since these trajectories are used to interpret quantum dynamics in a pictorial, classical-like language, it is instructive to examine them in detail.

III.2.C1 The Potentials

The "pseudo-classical potential" $v \equiv \langle G|V|G\rangle/\langle G|G\rangle$ appearing in (III.5b) can be written as

$$v = \pi^{-1/2} \cdot \int_{-\infty}^{+\infty} dy \exp[-y^2]\, V[R(t)+l(t)y] \qquad \text{(III.13)}$$

where $l(t) = [\hbar/2\mathrm{Im}\alpha(t)]^{1/2}$ is the width of the packet.

Since the greatest contribution to the integral comes from the values of y between zero and one the center of a packet located at R(t) is acted upon by the values of the classical potential between the points R(t) and R(t) + l(t), "averaged" with the Gaussian distribution $\exp(-y^2)$. A more precise statement can be made for the exponential potential $V(x) = \exp[-\lambda x]$ for which

$$v = \exp(-\lambda[R-\lambda l^2/4]) \; . \qquad \text{(III.14)}$$

Thus, for this particular case, the pseudo-classical potential acting on the center R(t) of the packet is equal to the classical potential at the point $R-\lambda l^2/4$. The packet moves as if it is a

"ball" with a time dependent "radius" $\lambda l^2/4$; its center interacts with the potential before it reaches the interaction region of the classical potential; and it turns around before it reaches the classical turning point. Note that the "radius" of the "ball" varies in time and depends on both the width of the Gaussian and the rate of spatial variation of the potential at the site where the packet is located.

The physical origin of this behavior is the same as that of the Heisenberg uncertainty relation. The "radius" of the packet is given by $l^2/2 = \langle G|(x-R)^2|G\rangle/\langle G|G\rangle$ which is a measure of the quantum fluctuations of the position operator in the Gaussian state. To bring the classical and the pseudo-classical potentials into agreement we must have $l(t) \to 0$, which means $\mathrm{Im}\alpha \to \infty$. In this case, however, the mean kinetic energy $\langle G|(-\hbar^2/2m)\partial^2/\partial x^2)|G\rangle/\langle G|G\rangle$ becomes infinite and so does the expectation value of the energy operator. This happens because the length l and the quantum fluctuations of the momentum are related through the Heisenberg relation ($\Delta p \cdot l \leq \hbar/\sqrt{2}$ with a minimum uncertainty equality when $\mathrm{Re}\alpha=0$).

The pseudo potential $v = \langle G|V|G\rangle/\langle G|G\rangle$ corresponding to the classical Morse potential (III.12a) is

$$v = D\{1+\exp[-2\lambda(R-x_0-\lambda l^2/2)] - 2\exp[-\lambda(R-x_0-\lambda l^2/4)]\} .$$

We compare v and V in Fig. 3 for various values of $\mathrm{Im}\alpha$ (i.e. l (t)) sampled from values that occur in the MEM calculations. Since l(t) varies in time in the course of packet propagation, v is time dependent. The drawings in Fig. 3 show the instantaneous values of the pseudo-potential for various values of l.

The values of the potential and the pseudo-potential energies as a function of time are shown in Fig. 4. These are obtained by propagating R and α according to the MEM and LHA

equations, respectively. Thus v depends on the MEM values R(t) and Imα(t), while V depends on the LHA (i.e., classical) values of R(t). It is important to note that the dependence of the pseudo-potential v on Imα(t) has no classical analog. The appearance of Imα(t) reflects the quantum fluctuations of the position operator which makes the average value of the classical potential different from the classical potential at the average position (i.e., $\langle G|V(\hat{x})|G\rangle \neq V(\langle G|\hat{x}|G\rangle)$ where $\hat{x}$ is the position operator). This reflects Heisenberg's uncertainty principle. If we want to think of the pseudo-classical motion in classical terms we must accept the fact that the variables P and R are coupled to a "classical time dependent field Imα(t)" whose time evolution is prescribed by the MEM equations (III.5).

The graphs in Fig. 4 show that the time evolution of the pseudo-classical and the classical potential energies v and V(R(t)), respectively, is rather different. A detailed analysis indicates that they differ both because MEM and LHA give different results for the time evolution of R(t) and because l(t), which enters in v but not in V, varies greatly in time. It is interesting to note several of the effects of the "field" Imα(t) on v which make its time evolution very different from that of V: v does not vary periodically in time; the point where v is maximum is not the turning point of R(t); the point where v is minimum is not the point of maximum kinetic energy.

III.2.C2 The classical and the pseudo-classical energies.

Further difference between the pseudo-classical and the classical mechanics can be seen by examining energy conservation in the two theories. Because the pseudo-classical equations resemble the classical ones we can apply to them the procedure used in classical mechanics to derive the energy conservation condition. That is we multiply $\dot{P} = -\partial v/\partial R$ with P/m, replace P/m by $\dot{R}$ in the right hand side and rewrite the equation in terms of

a total time derivative. The result is

$$\frac{d}{dt}\left(\frac{P^2}{2m} + v(R)\right) = \frac{\partial v}{\partial \mathrm{Im}\alpha} \cdot \frac{d\mathrm{Im}\alpha}{dt} \qquad \text{(III.16)}$$

The quantity $P^2/2m + v \equiv \mathcal{E}(t)$ is conserved only if $d\mathrm{Im}\alpha/dt = \dot{0}$ (i.e. frozen Gaussians) or $\partial v/\partial \mathrm{Im}\alpha = 0$.

In general the pseudo-classical energy $\mathcal{E}(t)$ is not conserved. There are several useful ways of stating the reason for this. Since the pseudo-classical potential v depends on the "external time dependent field" $\mathrm{Im}\alpha(t)$, the systems of equations (III5a-b) is not conservative; the "particle" (i.e. the trajectory) exchanges energy with the field. Another insight in the behavior of $\mathcal{E}(t)$ is gained by examining the total quantum energy of the state G:

$$\langle G|H|G\rangle/\langle G|G\rangle = \mathcal{E}(t) + \hbar|\alpha|^2/2m\mathrm{Im}\alpha \qquad \text{(III.17)}$$

Since this quantity must be conserved, the pseudo-classical energy $\mathcal{E}(t)$ varies in time to compensate for the time evolution of $\hbar|\alpha|^2/2m\ \mathrm{Im}\alpha$. The latter quantity is equal to $\langle G\,(\hat{P} - \langle G|\hat{P}|G\rangle)^2|G\rangle/2m\langle G|G\rangle)$ which is the momentum fluctuation in the state $|G\rangle$ ($\hat{P}$ denotes the momentum operator and $\langle G|\hat{P}|G\rangle = P(t)$). The presence of this term in the total energy is a purely quantum effect which reflects Heisenberg's uncertainty principle. The term is very large when the packet is localized in the coordinate representation.

The time evolution of $\langle H\rangle \equiv \langle G|H|G\rangle/\langle G|G\rangle$ for MEM and LHA is plotted in Fig. 5, together with $\mathcal{E}(t)$ given by the two theories. We see that $\langle H\rangle$ is conserved in MEM but not in LHA, which conserves the classical energy. In many cases it is useful to monitor $\langle H\rangle$ in LHA calculations since its change with time is a fairly sensitive indication that LHA is breaking down.

III.3 THE INDEPENDENT GAUSSIAN APPROXIMATION (IGA)

III.3.A The Description of the Approximation

This approximation is obtained by cancelling in the equations (A3-A7), (giving the time evolution of the parameters) all the integrals of the form $\int dx (x-R_A)^n (x-R_B)^m G_A^* G_B \equiv M(An|Bm)$ and $\int dx (x-R_A)^n G_A^*(x) V(x) G_B(x) \equiv V(An|Bo)$ in which A differs from B. In the compact matrix notation of the equations (A.9)-(A.12) this amounts to retaining only the diagonal part of the matrix $\overleftrightarrow{M}$ and eliminating the V(An|Bo) terms (A≠B) from $\vec{v}$. This decouples the components of the vector $\vec{X}$ and leads, after a little algebra, to the equations (III.5a-d) for each Gaussian. There is thus no coupling between the parameters belonging to different Gaussians.

The IGA achieves a considerable saving of both programming labor and computer time. Its validity is however suspect on physical grounds. On one hand, the assumption $\psi(x;t) = \Sigma G_A(x;\{\lambda(t)\})$ requires the Gaussians to add up coherently to the correct wave function at all times, while on the other hand IGA eliminates all the matrix elements through which the time dependent Schroedinger equation forces the Gaussians to influence each other. Unless very special circumstances are at work, it is hard to believe that independent Gaussians can act in concert to construct an accurate expression for ψ.

III.3.B The role of the coupling between Gaussians in the pseudo-classical mechanics.

To understand the implications and the consequences of IGA it is useful to examine the role of the neglected coupling from the point of view of the "mechanics" controlling the motion of the center of the packets. We continue to call this a pseudo-classical mechanics even though when a sum of Gaussians is used to represent $\psi(x;t)$ the resemblance to classical mechanics is diminished. The motion of one real, physical particle whose wave

function is described by a sum of N Gaussians is represented in the resulting pseudo-classical mechanics by the trajectories of N "pseudo-particles", tracing the motion of the centers of the Gaussians. In the MEM equations these trajectories are coupled to each other and to the "external time dependent fields" α_A and γ_A (i.e. the width and the phase of each Gaussian). IGA eliminates the coupling between the trajectories; LHA eliminates the coupling to the "external fields".

In what follows we examine the motion of the coupled pseudo-particles by considering two Gaussians only. That is, we consider the wave function $\psi(x;t) = G_A(x) + G_B(x)$ satisfying the time dependent Schrodinger equation with $H = -(\hbar^2/2m)\nabla^2+V(x)$, and look at the equations for $\dot{R}_A$, $\dot{P}_A$, $\dot{R}_B$ and $\dot{P}_B$. The latter are given by the third and the fourth rows of the matrix equation $\vec{X} = (\overleftrightarrow{M})^{-1}\cdot\vec{v}$ (see Eqs. (A.10-A.13)) and are

$$2\alpha_A(P_A/m - \dot{R}_A) + \dot{P}_A = (\overleftrightarrow{M}^{-1}\cdot\vec{v})_3 \equiv F_3 \qquad \text{(III.18)}$$

and

$$2\alpha_B(P_B/m - \dot{R}_B) + \dot{P}_B = (\overleftrightarrow{M}^{-1}\cdot\vec{v})_4 \equiv F_4 \qquad \text{(III.19)}$$

The right hand sides of these equations are very complicated complex functions (through M(An|Bm) and V(An|B0)) of all the parameters of the two Gaussians. Taking the real and imaginary parts of Eq. (III.18) we can solve for $\dot{R}_A$ and $\dot{P}_A$ to obtain

$$\dot{R}_A = P_A/m - (2\mathrm{Im}\alpha_A)^{-1}\ \mathrm{Im}F_3 \qquad \text{(III.20)}$$

and

$$\dot{P}_A = \mathrm{Re}F_3 - (\mathrm{Re}\alpha_A/\mathrm{Im}\alpha_A)\ \mathrm{Im}F_3 \qquad \text{(III.21)}$$

These equations take simpler forms under the conditions discussed below. The one-Gaussian terms in $\overleftrightarrow{M}$ and $\vec{v}$ (i.e., the

terms of the form $\int G_A(x)^* f(x)\, G_A(x)\, dx$, with $f(x)$ a real function such as $(x-R_A)^n(x-R_B)^m$ or $(x-R_A)^n V(x)$, are real and the two Gaussian terms, i.e., $\int G_A(x)^* f(x)\, G_B(x)\, dx$ with $A \neq B$, are complex. Therefore, if we neglect the imaginary parts of the two Gaussian terms we obtain $\mathrm{Im}F_3=0$ which leads to (from Eq. (III.20)) $\dot{R}_A = P_A/m$ which has the classical form. Furthermore, from (III.21) we obtain $\dot{P}_A = \mathrm{Re}F_3$ where F_3 depends on the parameters of all the Gaussians. This is very different from the classical equation of motion $\dot{P}_A=-\partial V(R_A)/\partial R_A$ and from the pseudo-classical equation for one Gaussian $\dot{P}_A = - \langle G|\partial V/\partial x|G\rangle/\langle G|G\rangle$. A further simplification can be obtained by setting all two Gaussian integrals equal to zero (i.e., we make the IGA). In that case we obtain the equations (III.5a-d) for each Gaussian. A complete decoupling occurs and each Gaussian evolves independently according to the pseudo-classical equations (III.5). Thus, within the IGA the wave function can be described as composed of the coherent sum of packets whose centers are moving independently on the potential surface according to the pseudo-classical equations of motion under the influence of a force given by the time dependent mean potentials $v_A \equiv \langle G_A|V|G_A\rangle/\langle G_A|G_A\rangle$ and $v_B \equiv \langle G_B|V|G_B\rangle\langle G_B|G_B\rangle$. The widths and the phases of these Gaussians are also uncorrelated.

As we have already mentioned, the pseudo-classical mechanics generated by a two packet wave function deals with two "pseudo-particles" moving on two coupled trajectories. Each pseudo-particle has its own potential V_A or V_B, which depends on the time dependent fields $\mathrm{Im}\alpha_A$ and $\mathrm{Im}\alpha_B$; besides, the pseudo-particle A is acted upon by forces neglected by IGA which depend on P_B-P_A, R_A-R_B, $\mathrm{Im}\alpha_A-\mathrm{Im}\alpha_B$, $\mathrm{Re}\alpha_A-\mathrm{Re}\alpha_B$ and $\gamma_A-\gamma_B$. The non-classical nature of such forces is obvious.

It is interesting to note that in the early days of quantum mechanics it was popular to represent the time evolution of one particle wave functions in terms of the flow of a continuous

distribution of classical like "particles" endowed with well defined trajectories and momenta and interacting through an effective stress tensor.[19] The multiple trajectory pseudo-classical representation proposed here is in many ways similar to the representations proposed in these early works.

The use of multiple Gaussian wave functions can be easily justified by the greater flexibility (i.e. larger number of parameters in the least square fit) of the basis set, which gives hope for greater accuracy. There are however many important situations when the use of multiple, coupled Gaussians must be used even if a crude but qualitatively correct description of the scattering process is desired. This happens in multiple channel problems in which the channels are not overlapping in either the coordinate or the momentum space. One example, provided by surface-atom scattering, is the case when one channel is a particle trapped at the surface and the other is a particle back-scattered into the vacuum. Another example is provided by the curve crossing problems in which an atom in the "ionic" channel has in the classical limit a different momentum than the atom in the "neutral" channel. Such events cannot be described - even qualitatively - by one Gaussian packet. Therefore, in such situations the multi-pseudo-particle description of the dynamics is the only reasonable "classical like" picture of the quantum process.

III.3.C The validity conditions for IGA.

Given the great simplification introduced by IGA it is important to have a clear idea under what circumstances we expect it to work. We discuss first the case when IGA is used together with the local harmonic approximation (LHA) (we call this the simple Heller method (SHM)) and show that if LHA is made then the wave packets become decoupled and IGA is exact. We consider this to be a rather striking result since we could not find

intuitively any link between the two approximations: one of them has to do with the relationship between the width of each individual Gaussian and the rate of change of the potential with x; the other with the overlap between different Gaussians. Since we believe that LHA is likely to fail in some (or many?) practical cases the above observation is not of much practical help. It does however explain why Heller was so successful while using the IGA method in problems involving harmonic oscillators. If LHA is not made one can show that the Gaussians might become decoupled when the packets do not overlap, or when they have very different momenta, or when their phases vary extremely rapidly in time.

III.3.C1 The simple Heller method (SHM = LHA + IGA)

There is numerical evidence that harmonic oscillators have special properties with respect to the Gaussian propagation method discussed here. One of the very first calculations carried out by Heller studied the excitation of a harmonic oscillator hit by an atom. He described the initial oscillator wave function as a sum of Gaussians, used SHM to propagate them and obtained satisfactory results. One the other hand both Skodje and Truhlar[16] and Heather, Jackson and Metiu[17] have shown that SHM or IGA gives inaccurate results when applied to propagate states of a Morse oscillator. This is the case even for low energy states which are nearly harmonic.

In order to understand why Heller's calculation was so successful we have investigated the effect of LHA on the coupling between Gaussians. We have found that LHA decouples the Gaussians exactly. As a corollary, in the case of a harmonic oscillator, where LHA is exact, the simple Heller model (LHA and IGA) is exact!

To show how this is proven we consider, as an example, the

equation (A.5). For two Gaussians this can be written as:

$$(P_A^2/2m - P_A\dot{R}_A - i\hbar\alpha_A/m + \dot{\gamma}_A)\, M(B1|A0) + \qquad \text{(III.22)}$$

$$[2\alpha_A(P_A/m-\dot{R}_A) + \dot{P}_A]\, M(B1|A1) +$$

$$[2\alpha_B(P_B/m - \dot{R}_B) + \dot{P}_B]\, M(B2|B0) +$$

$$[\dot{\alpha}_A + 2\alpha_A^2/m]\, M(B1|A2) +$$

$$V(B1|A0) + V(B1|B0) = 0 \ .$$

The notations M and V have been specified in the Appendix A.

The discussion proceeds now as follows. Let us assume that the two Gaussians move according to the simple Heller model (SHM); that is the quadratic approximation of the potential is made and the Gaussians are assumed to be independent. This means that we assume the SHM equations (III.5a) and (III.7b-d) for the parameters $\dot{R}_A$, $\dot{P}_A$, $\dot{\gamma}_A$ and $\dot{\alpha}_A$ and $\dot{R}_B$, $\dot{P}_B$, $\dot{\gamma}_B$ and $\dot{\alpha}_B$. If these equations are inconsistent with (III.22) then by introducing them in (III.22) we must obtain a non-zero result whose magnitude indicates the extent of the error made by SHM. Making the substitution just mentioned leads to

$$\text{Error} \equiv - V(R_A) \int(x-R_B)G_B^*G_A dx - (\partial V/\partial R_A)\int(x-R_B)(x-R_A)G_B^*\, G_A dx$$

$$-(\partial V/\partial R_B)\int(x-R_B)^2G_B^*G_B dx - (1/2)(\partial^2 V/\partial R_A^2)\int(x-R_B)(x-R_A)^2G_B^*G_A\, dx$$

$$+\int(x-R_B)G_B^*VG_A dx + \int(x-R_B)G_B^*VG_B dx = 0 \quad . \qquad \text{(III.23)}$$

Now let us make the local harmonic approximation to evaluate the integrals present in the error expression. If we expand V(x) in the last integral in powers of $(x-R_B)$ and V(x) in the integral before the last in powers of $(x-R_A)$, we find that the error is

exactly zero (if we retain only the quadratic terms in the expansion). Therefore once we accept LHA the independence of Gaussians follows!

III.3.C2 The General Case

While in general the coupling between Gaussians must be taken into account, there are several situations in which it can be neglected, even if LHA is not made.

(α) The most obvious one is when the Gaussians do not overlap. This can happen when dealing with problems in which the wave function tends to split into spatially separated pieces. A trivial example is the low energy state of a double well potential. A more interesting one is provided by atom scattering from a moving surface. There is a finite probability that during the collision the incident particle excites phonons and is trapped at the surface; there is also a finite probability that the particle is scattered back into the vacuum. Therefore the atomic wave function "splits" into a component bound to the surface and an outgoing free particle component. If the wave function is approximated by two Gaussians they will best mimic this situation if one of them is trapped at the surface and the other is reflected. Except for the early times during the collision, when nothing much happens, the overlap between these Gaussians should be fairly poor and a calculation ignoring the coupling between them has a fair chance of success.

(β) Another interesting situation takes place when the integrands in the quantities M(An|Bm) and V(An|BO) appearing in the equations of motion (A.9-12) (or the Equation (III.22) which is one particular example) oscillate very rapidly around zero. Since all such terms are of the form $\int dx\, G_A^* G_B f(x)$ with f(x) a real function (of the form $(x-R_A)^n (x-R_B)^m$ or $(x-R_A)^n V(x)$) the oscillatory behavior arises from the phase of the product $G_A^* G_B$. If the wave length of this oscillation is much smaller than the width of the Gaussian $G_A^* G_B$ the integral is practically zero.

One term in the phase of $G_A^* G_B$ is $[(P_B-P_A)/\hbar]x$, which gives the wave vector $k = (P_B - P_A)/\hbar$. Since the width of $G_A^* G_B$ is $l = l_A l_B/(l_A^2+l_B^2)^{1/2}$, the integral tends to zero if $2\pi/k << l$. This is easy to understand on physical grounds. If P_B and P_A are very different, the packets G_A and G_B are segments of planar waves having very different wavelength. As is well known such waves are poorly coupled, which means that their matrix elements $\int G_A^* f(x) G_B dx$ are very small.

(γ) Finally, we point out that it is possible that two Gaussians become decoupled if their two-Gaussian integrals oscillate rapidly around zero with time. To explain this we can use Eq. (III.22) as an example. The integrals M(An Bm) and V(An'B0) are complex and therefore have the form $a(t)e^{-i\phi(t)}$, where a(t) and $\phi(t)$ are real functions of time. The structure of these integrals is such that they will have the same phase since that is determined by $G_A^* G_B$ which appears in all integrands. To simplify matters consider the schematic representation of Eq. (III.22) provided by

$$a(t)e^{-i\phi(t)}X_1(t) + M(t)X_2(t) = V(t) + e^{-i\phi(t)}b(t) \quad \text{(III.24)}$$

Here the terms with the phase $\phi(t)$ are two-Gaussian integrals, M(t) and V(t) are one-Gaussian integrals and $X_1(t)$ and $X_2(t)$ are combinations such as $2\alpha_B(P_B/m - \dot{R}_B) - \dot{P}_B$ or $\dot{\alpha}_A - 2\alpha_A^2/m$, etc. If we can neglect all the two-Gaussian integrals then the Gaussians become decoupled. Consider now a situation in which $\phi(t)$ varies in time faster than all other quantities. If we analyze the behavior of the Eq. (III.24) in the neighborhood of a time t_o we can expand $\phi(t) = \phi(t_o) - (\partial\phi(t_o)/\partial t_o)(t-t_o)$. The exponential term $e^{i\phi(t)}$ oscillates (in the neighborhood of t_o) with the period $T = 2\pi/[\partial\phi(t_o)/\partial t_o]$. If this is smaller than the time scale τ over which $X_1(t)$, M(t), V(t), a(t) and b(t) change appreciably we can integrate the equation (III.24) from $t_o - T/2$ to $t_o - T/2$ and obtain $M(t) X_2(t) = V(t)$. Thus the two

Gaussian integrals which cause the coupling between the Gaussians disappear from the equation of motion and the Gaussians evolve independently. We see that pseudo-classical motion behaves just like the classical one: it tends to ignore forces that act at frequencies vastly different than the rate of change of the parameters being propagated.

One can derive an expression for $\phi(t)$ and show that in the cases when the two Gaussians overlap well $\phi \simeq \mathrm{Re}\gamma_B - \mathrm{Re}\gamma_A$; thus the phase of the integrals is proportional to the difference between the phases of the two Gaussians. Within LHA these phases are proportional to the classical actions along the trajectories of the centers of the two Gaussians. So, two Gaussians following trajectories having classical actions that change rapidly in time, are weakly coupled.

IV. The Choice of Initial Wave Function

IV.1 Introductory Remarks

The choice of the initial wave function is in principle very simple: it must fit as closely as possible the experimental conditions of interest. The practical implementation of this idea in the context of GWP propagation was done in a manner which causes ambiguities and (sometimes) trouble.

The first difficulty appears because of the practice of writing the initial wave function as a sum of Gaussians in a way that leaves us free to choose certain parameters (i.e. width, momentum, etc.) almost at will. This "asymptotic freedom" permits us sometimes to affect substantially and arbitrarily the final wave function; this is not a desirable feature in any theory.

The second difficulty is more subtle and is common to all methods using a pre-selected basis set to represent the wave function throughout the collision process. A set might be flexible enough to represent the initial state well, but be incapable to describe the intermediate or the final wave function with the desired accuracy. The problem is particularly interesting in cases with many channel final states of the kind that can be intuitively described by multiple classical trajectories that cover different regions of configuration space. Such situations cannot be represented by a single Gaussian packet. The desired flexibility can be achieved by increasing the number of Gaussians used to fit the wave function. There is however a limit to this and our experience, drawn from a variety of numerical studies, is that we cannot mindlessly add more and more Gaussians until the results converge, since in the course of collision the Gaussians often overlap causing over-completeness; when this happens the differential equations propagating the parameters become singular and intractable.

IV.2 The Asymptotic Freedom

To understand how this problem arises it is best to examine several examples. The first is the representation of a planar wave as a sum of Gaussians, which has been used in all the GWP diffraction calculations published so far.[10,18] We start with the identity[10]

$$k_z^{-1/2}\ \exp[i\vec{k}\cdot\vec{r}] = C \int d\vec{r}'\ \exp\{(i/\hbar)\ (\vec{r}-\vec{r}')\cdot\overleftrightarrow{A}\cdot(\vec{r}-\vec{r}') + i\vec{k}\cdot(\vec{r}-\vec{r}') - i\vec{k}\cdot\vec{r}'\} \tag{IV.1}$$

where C is a normalization constant.

To obtain an approximate representation of the planar wave as a sum of Gaussians we discretize the integral. This gives

$$k_z^{-1/2}\ \exp[i\vec{k}\cdot\vec{r}] = C \sum_p \exp\{(i/\hbar)[(\vec{r}-\vec{r}_p)\cdot\overleftrightarrow{A}\cdot(\vec{r}-\vec{r}_p) + \vec{k}\cdot(\vec{r}-\vec{r}_p) + i\vec{k}\cdot\vec{r}_p\}. \tag{IV.2}$$

The number of Gaussians and their mean positions are fixed by the accuracy we impose when we represent the integral by a sum. The momentum of each packet is $\hbar\vec{k}$ and the phase is real and given by $\vec{k}\cdot\vec{r}_p$. However the method gives no prescription for fixing the initial values of the width matrix $\vec{A}$. It is reasonable to take the initial off diagonal elements zero and assume that the diagonal ones are equal, because of the isotropy of space. These decisions still leave the complex diagonal element α of the width matrix unspecified.

The exisiting practice has been to argue that since (IV.2) represents the initial state well for any reasonable choice of α, we can use the "asymptotic freedom" to select a value of α that would make our life simpler. If we plan to use SHM (which has

been the case so far) we should select Imα so that the packet will be narrow when it collides with the hard wall of the potential. This should increase the accuracy of LHA (which is used in SHM). However since Imα(t) is controlled by the equations of motion we can not fix its value at the wall by selecting the initial value. The practice has been to use the equation of motion for Imα(t) in free space and to select Imα(0) such that Imα(t) at the wall location would be large if the packet moves in free space. While this gives some guidance concerning the choice of Imα(o) it leaves Reα(o) unspecified and this is taken to be zero.

Unfortunately detailed numerical studies[18] show that this choice of the width does not achieve its stated goal: no matter how we choose Imα(o) the potential broadens the packet beyond the values for which LHA can be safely applied. Furthermore, we find that the final results depend sometimes on the choice of Imα(o). While in the case of diffraction changing Imα(o) does not lead to large deviations from the known quantum results, we feel rather uncomfortable in using such a strategy for cases where the "exact" results are unknown.

Another example is Heller's integral representation of a harmonic oscillator wave function

$$\psi_n(y) = C_n \int_o^T dt \exp\{-(\frac{m\omega}{2\hbar})\ (y-y(t))^2 + (i/\hbar)p(t)(y-y(t)) + (i/2\hbar)(p(t)y(t) - p(o)y(o)) + in\omega t\} \qquad \text{(IV.3)}$$

Here p(t) and y(t) satisfy the classical equations of motion of the oscillator momentum and position, $T = 2\pi/\omega$, and p(o), y(o) are the initial conditions for the momentum and position of the oscillator. We can now represent $\psi_n(y)$ as a sum of N Gaussians by discretizing the integral. This gives

$$\psi_n(y) = C_n \sum_{\alpha=1}^{N} \exp\{-(m\omega/2\hbar)[y-y(t_\alpha)]^2 + (i/\hbar)\, p(t_\alpha)[y-y(t_\alpha)] + (i/2\hbar)(P(t_\alpha)y(t_\alpha) - p(o)\, y(o)) + in\omega t_\alpha\}\,, \tag{IV.4}$$

with $t_\alpha = (2\pi\alpha)/(N\omega)$.

The prescription tells us that the points $p(t_\alpha), y(t_\alpha)$ lie on the classical trajectory at equally spaced time intervals. The initial p(o), y(o) are not however specified so the phase of the classical oscillatory motion giving p(t), q(t) is arbitrary.

A similar situation occurs in the representation of the rotational wave functions, where group theory tells us how to construct the wave function as a sum of Gaussians whose centers are located on the surface of a sphere. The other parameters in the Gaussians remain at our disposal. In more general cases the asymptotic wave functions $\phi_n(x;0)$ are represented as linear combinations of N Gaussians

$$\phi_n(x;0) = \sum_{A=1}^{N} C_{An}\, G_A(x;\{\lambda(0)\}_A) \tag{IV.5}$$

whose parameters, symbolized in (IV.5) by $\{\lambda(o)\}_A$, are chosen before the linear coefficients C_{An} are determined. The latter are found by minimizing the total energy of the asymptotic system; in the course of this minimization the parameters $\{\lambda(0)\}_A$ are frozen. This procedure also suffers from the fact that it provides no objective method for chosing $\{\lambda(0)\}_A$.

In what follows we discuss a procedure which is more efficient and more satisfactory conceptually and practically: we represent the initial wave function $\phi_n(x;0)$ by a sum of Gaussians whose parameters are chosen by a non-linear least square fitting (LSF) procedure. That is, we minimize

$$F(\{\lambda\}_{A=1},\ldots,\{\lambda\}_{A=N}) \equiv \int dx\, \chi(x)\left|\left(\phi_n(x;o) - \sum_{A=1}^{N} G_A(x;\{\lambda\}_A)\right)\right|^2 \qquad (IV.6)$$

with respect to the parameters $\{\lambda\}_A$. The idea is so simple that it would not merit further discussion except for the fact that it brings about a number of dramatic improvements.

(α) The number of Gaussians required for obtaining a good fit by Eq. (IV.6) is much smaller than that required by other methods. Consider for example the fit of a low lying Morse state by using Eq. (IV.5). We can make a reasonable choice of Gaussians as follows. If we assume that the low lying Morse states are nearly harmonic we can use Heller's equation (IV.4) to select the parameters $\{\lambda\}_A$ (i.e. position, momentum and phase) in $G_A(x;\{\lambda\}_A)$. Taking linear combinations of these Gaussians, like in (IV.5), we can find the linear coefficients C_{An} by minimizing the energy with respect to them and keeping $\{\lambda\}_A$ frozen. We can get very good fits of the low lying states by using eight Gaussians. By using Eq. (IV.6) we obtain an equally good fit with only two Gaussians.

(β) The non-linear least square fit method has the advantage that it fixes all the parameters objectively. The number of Gaussian is predetermined by the choice of the error that we are willing to tolerate in the initial wave function and the flexibility required during propagation.

(γ) It is interesting to note that lowering the number of Gaussians is not a matter of efficiency only. We find that it is very difficult to propagate wave functions composed of a large number of coupled Gaussians because in the course of their evolution they can overlap and the set becomes overcomplete. As a result the differential equations propagating the parameters become nearly singular and give very large errors. As an example

propagated a linear combination of eight Gaussians representing the third Morse state and a three Gaussian non-linear least square fit (i.e. Eq. IV.6) to the same function. In the first case the computer fails to solve the MEM differential equations propagating the parameters, because the matrix $\overleftrightarrow{M}$ coupling the Gaussians becomes singular. The reason for this seems to be the overcompletness of the set, which we detect by diagonalizing the matrix formed with the Gaussian overlap integrals; the singular behavior of $\overleftrightarrow{M}$ is always preceeded by the decrease of one or more of the eigenvalues of the overlap matrix. A calculation using a sum of three Gaussians to fit non-linearly the initial Morse state has no difficulty.

It is important to note that the non-linear fitting is not entirely free of ambiguities, since several "best fits" can be obtained, depending on the starting point and the minimization strategy pursued. Consider for example the third Morse eigenfunction which the non-linear least square fit program can represent very well by a sum of three Gaussians. Let us assume now that we decide to try a four Gaussian fit. We find that for certain starting parameters the LSF program makes the amplitude of one Gaussian nearly zero and fits the wave function with the remaining three Gaussians. Even though we get a very good fit this sum is a very bad initial function since the MEM program cannot propagate it; the matrix $\overleftrightarrow{M}$ in Eq. (A.10) is nearly singular because of poor overlap between the nearly zero amplitude Gaussian and the others. However it is quite possible to get a satisfactory four Gaussian initial wave function if we constrain the width $\mathrm{Im}\alpha_A$ and the normalization $\mathrm{Im}(\gamma_A)$ for each Gaussian to stay within reasonable limits. The MEM program propagates this function rather well.

IV.3 The Optimum Number of Gaussians

In many cases we would like to use the smallest number of Gaussians, and for this the non-linear LSF of the initial wave function is very helpful. There are however cases when such a choice would be physically unsound. Consider a Morse oscillator colliding with an atom. We can fit the initial wave function (the ground state of the Morse oscillator) well with one Gaussian. However, if the kinetic energy of the incident atom is comparable, but smaller, than the dissociation energy, the final state is a linear combination of several Morse functions. One Gaussian cannot describe correctly such a wave function; it can at best give the average energy transferred but we could not expect correct state occupation amplitudes. It is therefore a good idea to try to fit the initial state with several Gaussians. This is a general situation in most cases in which the final state is very different from the initial one.

Another situation requiring a fit to many Gaussian functions is that in which the final state has several channels which are qualitatively different. One simple example is atom surface collisions in which surface trapping is of comparable likelihood with surface reflection.

These situations are too subtle and rich in physical consequences to be treated profitably in the general setting of this paper. Several specialized studies of photodissociation, vibrational excitation of diatomics, curve crossing and surface trapping, which provide interesting and detailed illustrations for the importance of chosing correct multiple Gaussians representations of the wave function, will be published shortly.

V. FINAL STATE ANALYSIS

Generally scattering theory requires the knowledge of the eigenstates of the zero order Hamiltonian and the computation of various matrix elements involving them.. One of the advantages of the Gaussian wave packet approach is that we can calculate easily the matrix elements needed for the propagation of the wave function: most potential energy functions can be fitted to polynomials, exponentials, Gaussians, or to sums or products of such functions, so the integrals can be done easily: the matrix elements of the kinetic energy operator require the calculation of integrals involving a product of Gaussians and polynomials.

Part of this advantage is however lost if we must analyse the scattered wave functions by calculating the matrix elements $\int \phi_n(x)\psi(x,t)dx$ with the eigenstates of the final zero-th order Hamiltonian. From a practical point of view in many situations we don't have simple formulae for $\phi_n(x)$ and we must generate them numerically, which makes the calculation even more tedious. And sometimes $\phi_n(x)$ are known only very approximately.

We present below a very simple and rather general idea that permits the analysis of the final wave function by using the program that propagates the MEM equations. Since the overlap of planar waves with Gaussian functions is a Guassian in momentum space we need no special procedure for the analysis of the final translational state. We concentrate therefore on analysing the internal states only.

Let us assume that at the time t_o when the projectile target interaction stopped we have a scattered wave function (internal state) given by

$$\psi(x;t_o) = \sum_A G_A(x;\{\lambda(t_o)\}_A) \quad . \qquad (V.1)$$

We can use the MEM equations to propagate this wave function with

the zero order Hamiltonian of the internal states. If we denote by $\psi(x;t)$ the propagated wave function we can easily show that

$$C(\omega) \equiv \int_{t_o}^{\infty} dt\, e^{+i[\omega - i\lambda](t-t_o)} \int \psi^*(x;t)\, \psi(x;t_o)\, dx \qquad (V.2)$$

satisfies

$$\text{Re } C(\omega) = \sum_{n=0}^{\infty} \frac{|C_n|^2 \lambda}{(\omega-\omega_n)^2 - \lambda^2} \qquad (V.3)$$

and

$$\text{Im } C(\omega) = \sum_{n} |C_n|^2 \frac{(\omega-\omega_n)}{(\omega-\omega_n)^2 + \lambda^2} \qquad (V.4)$$

Here n runs over the bound (internal) states of the system. $|C_n|^2$ is the occupation of n-th state (i.e. the probability that the scattering process takes the system into its n-th state) and $\hbar\omega_n$ is the energy E_n of that state. The quantity λ is at our disposal. If we make it much smaller than ω_n the peaks in $\text{Re}C(\omega)$ are well separated and ω_n are given by peak positions and $|C_n|^2$ by the peak height. The zeroes of Im $C(\omega)$ are close to ω_n. However, if λ is too small then we must propagate the wave function $\psi(x;t_o)$ for a long time t such that $t\lambda >> 1$. A compromise can be reached by using an intermediate value for λ and determining $|C_n|^2$ and ω_n by a least square fit of $C(\omega)$ to the forms (V.3) and (V.4).

From a physical point of view the quantity $C(\omega)$ is a Green's function for a fictitious absorption process (or fluorescence) which is used to resolve the post-collision state $\psi(x;t)$ into spectral components.

Sometimes the propagation procedure is not reliable enough to be comfortably used for a very long time. In such occassions, we can define $C_T(\omega)$ by using Eq. (V.2) with the upper integration limit equal to T. It is easy to show that

$$\mathrm{Re}C_T(\omega) = \sum_n |C_n|^2 \lambda[(\omega-\omega_n)^2 + \lambda^2]^{-1}(1 - \lambda^{-1}e^{-\lambda T} [\lambda\cos(\omega-\omega_n)T + (\omega-\omega_n)\sin(\omega-\omega_n)T]) \tag{V.5}$$

and

$$\mathrm{Im}\ C_T(\omega) = \sum_n |C_n|^2 (\omega-\omega_n)[(\omega-\omega_n)^2+\lambda^2]^{-1}(1-(\omega-\omega_n)^{-1}e^{-\lambda T} [\lambda\sin(\omega-\omega_n)T + (\omega-\omega_n)\cos(\omega-\omega_n)T) \tag{V.6}$$

We can use these equations and a least square fit procedure to find ω_n and $|C_n|^2$.

By using a fast Fourier transform we find that this procedure is both efficient and reliable. An example was shown in Fig. 7. This was obtained as follows: we made the linear combination

$$\psi(x;t_o) = a_o\phi_o - a_1\phi_1 - a_2\phi_2 + a_3\phi_3$$

where ϕ_n is the n-th Morse eigenfunction; we then fitted this function to four Gaussians and pretended that this is our post-collision function; we propagated the Guassians with the Morse Hamiltonian and the MEM equations (solid curves). The graph shows ReC(ω) calculated by using Eq. (V.2). The least square fit analysis of these curves gives the eigenvalues and spectral composition $|a_o|^2,\ldots,|a_3|^2$.

VI STABILITY PROBLEMS IN THE PROPAGATION OF THE MEM EQUATIONS

VI.1 Introductory remarks.

In principle MEM would permit the propagation of hundreds of Gaussians, making many localized time dependent quantum problems within the reach of today's computer power. Unfortunately our numerical experience has revealed some limitations which are summarized in this section.

The first limitation is a numerical instability in the propagation of the Gaussian's widths. This was encountered by Heller in his use of SHM and he circumvented it by using what we call here a P-Z transformation. We show that, not unexpectedly, the same difficulty is present in MEM and that, fortunately, the MEM equations can be written in a form which permits the application of the P-Z method.

The second limitation appears when we attempt to use a large number of Gaussians. We find that in the course of time the Gaussians often evolve in a way that makes one (or more) of them redundant. When this happens the MEM equations become singular and cannot be solved. Superficially this may seem a pleasant problem, to be solved by reducing the initial number of Guassians. Unfortunately the optimum number of Gaussians is not a uniform function of time: as the collision proceeds the wave function contracts or spreads (in coordinate and/or momentum representation) so that the number of necessary Gaussians goes up and down in time. While at some given time N Gaussians may be too many and cause trouble, they may be needed at other times. We found no simple, general method of dealing with this problem, but we designed a useful strategy that is present here.

Since in most problems of interest to us the exact quantum solution is not known we test for errors in the propagat.. scheme by looking for internal inconsistencies. Practically we

use three criteria: (1) we require $\langle\psi(t)|\psi(t)\rangle$ to be time independent; (2) we require $\langle\psi(t)|H,\psi(t)\rangle$ to be time independent; and (3) we require $\int dt \exp[\pm i\omega t - \lambda t] \langle\psi(t)|\psi(o)\rangle$ (which satisfies Eqs. (V.3-4)) to give values of $|C_n|^2$ which add up to one (when $\langle\psi(t)|\psi(t)\rangle = 1$) and correct values for the eigenenergies $\hbar\omega_n$.

VI.2 The P-Z Transformation

The P-Z transformation was designed by Heller to solve difficulties connected with the propagation of the width matrix $\overleftrightarrow{\alpha}$. In SHM the difficulty appears in the equation $\dot{\alpha} = -2\alpha^2/m - (1/2)\,\partial^2 V/\partial R^2$ (Eq. (III.7)) propagating the width parameter α. This has an oscillatory behavior which causes a lot of trouble if we apply usual numerical methods (i.e. Runge-Kutta or predictor-corrector) to Eq. (III.7). In the best situations this can be cured by using an extremely small time step. In other cases erroneous values are obtained even for the smallest time steps. Our experience has been that both diffraction and curve-crossing calculations with SHM require the use of the P-Z method.

The MEM calculations carried out by us so far show that a direct, numerical solution of the MEM equations lead to dramatic failures, much more rapidly and frequently than in the case of SHM.

Fortunately the P-Z transform can be applied directly to the MEM equations if they are written in the proper form. We start with the equations (A.10-13) written as

$$\dot{\vec{X}} = (\overleftrightarrow{M})^{-1} \cdot \vec{v} \equiv \vec{F} \qquad \text{(VI.1)}$$

The only equations in the above system that require modification are those containing the components of $\dot{\vec{X}}$ having the form $\dot{\alpha}_A$ -

$2\alpha_A^2/m$. For example, in the one-dimensional two-Gaussian case discussed in Appendix A, there are the components X_5 and X_6 in Eq. (A.11). For three-dimensional Guassians these equations have the matrix form

$$\dot{\overleftrightarrow{\alpha}}_A + 2\frac{\overleftrightarrow{\alpha}_A \cdot \overleftrightarrow{\alpha}_A}{m} = \vec{F}_A(t) \qquad \text{(VI.2)}$$

where $\overleftrightarrow{\alpha}$ is the three dimensional matrix appearing in the term $(i/\hbar)\ (\vec{x} - \vec{R}(t)) \cdot \overleftrightarrow{\alpha} \cdot (\vec{x} - \vec{R}(t))$ at the exponent of each of the three dimensional Gaussian; $\vec{F}_A(t)$ is a known function of time.

We can remove the non-linear term $2\ \overleftrightarrow{\alpha}_A \cdot \overleftrightarrow{\alpha}_A/m$ by introducing two new variables $\overleftrightarrow{Z}$ and $\overleftrightarrow{P}$ (where $\overleftrightarrow{P}$ is not to be confused with the momentum) through

$$\overleftrightarrow{\alpha} = \overleftrightarrow{P} \cdot \overleftrightarrow{Z}^{-1}/2 \ . \qquad \text{(VI.3)}$$

The time derivative of $\overleftrightarrow{\alpha}$ is given by

$$\begin{aligned} 2\dot{\overleftrightarrow{\alpha}} &= \dot{\overleftrightarrow{P}}\ \overleftrightarrow{Z}^{-1} + \overleftrightarrow{P}\ d(\overleftrightarrow{Z}^{-1})/dt \\ &= \dot{\overleftrightarrow{P}}\ \overleftrightarrow{Z}^{-1} - \overleftrightarrow{P} \cdot \overleftrightarrow{Z}^{-1}\ \dot{\overleftrightarrow{Z}}\ \overleftrightarrow{Z}^{-1} \end{aligned} \qquad \text{(VI.4)}$$

If we now define

$$\dot{\overleftrightarrow{Z}} \equiv \overleftrightarrow{P}/m \ . \qquad \text{(VI.5)}$$

and use (VI.3-5) in (VI.2) we obtain

$$\dot{\overleftrightarrow{P}} = 2\overleftrightarrow{F} \cdot \overleftrightarrow{Z} \qquad \text{(VI.6)}$$

The P-Z methods solves (VI.5) and (VI.6) and uses the results to compute $\overleftrightarrow{\alpha}$ from (VI.3).

We find that the use of this procedure cures dramatically

some of the problems appearing when we try to solve (VI.2) directly.

VI.3 The singular behavior of the MEM equations

To solve the MEM equations we must invert the matrix $\overleftrightarrow{M}$ appearing in (A.10). Its elements are various moments $M(B_n|A_m)$ of the Gaussians used to fit the wave function. For a one-dimensional two-Gaussian wave function the matrix $\overleftrightarrow{M}$ is given by (A.12). The left-hand upper corner of that matrix is the overlap matrix between the Gaussians used to make the fit. This suggests that if the overlap matrix becomes singular it may be difficult to invert $\overleftrightarrow{M}$. Empirically we find this to be the case. As we solve the equations of motion for the parameters we also solve for the eigenvalues of the overlap matrix. We find that whenever one eigenvalue becomes very small the determinant of $\overleftrightarrow{M}$ becomes small and large propagation errors appear. For problems with a small number of parameters it is better to diagonalize $\overleftrightarrow{M}$.

There are a variety of methods which we use to cure this problem. (a) In some cases the problem is created by the way in which the sum of Gaussians represent the initial state. As a simple example consider the case when we want to fit a very broad Gaussian G with four narrower Gaussians G_A A=1,...4. We do this by varying the parameters in the Gaussian so that $E = \|G - \sum_A G_A\|$ is minimized. If we do not interfere, the minimization program might decide to vary the parameters in G_1 and make it identical to G, while simultaneously making $Im\gamma_2$,... $Im\gamma_4$ so large that G_2, G_3, G_4 have very small values. Any attempt to propagate the function $\sum_A G_A$ obtained in this way by MEM leads immediately to catastrophic errors. One can easily prevent the above events by minimizing E and keeping $Im(\gamma)_A$ below a preset value. The type of behavior exemplified above tends to be general. We find, for example, that as we increase the number of Gaussians used to fit the second excited state of a Morse

oscillator an unconstrained four Gaussian fit makes the amplitude of one Gaussian very small and the propagation of the resulting wave function fails very rapidly. If we constrain the amplitudes we get a four Gaussian fit which can be propagated successfully.

We note that symmetry can play an equally important role. For example, consider an initial wave function which is symmetric around R_0. A four Gaussain fit might use one Gaussian centered at R_0 and two placed symmetrically, and make the amplitude of the fourth nearly equal to zero. If we keep the centers of the Gaussians symmetrical around R_0, all four Gaussians are used but the fit may be of poor quality if, for example, the wave function peaks at R_0.

While such poor starts can be easily identified and cured, there are cases when in the course of its time evolution the spatial extent of the wave function shrinks causing more serious difficulties. If N Gaussians are required to fit the wave function at times when it has a large spatial extent, they may be redundant when the function shrinks. In such a case the propagation program may either make the Gaussians linearly dependent or make the amplitude of one of the Gaussians zero. In all these cases we find that the propagation gives large errors or stops altogether.

A cure for this problem can be provided by monitoring the evolution of the overlap matrix (or the $\overleftrightarrow{M}$ matrix) eigenvalues in time and by removing one Gaussian, when one eigenvalue becomes small. This can be done by fitting the current N Gaussian wave function $\psi(x;t) = \sum_A^N G_A(x;(\lambda(t))_A)$ to N-1 Gaussians whose parameters $(\lambda'(t))_A$ are fitted to minimize $\epsilon = \| \sum_A^N G_A(x;(\lambda)_A) - \sum_A^{N-1} G_A(x;(\lambda')_A) \|$. This removes the problem but it can create a new one latter: if the wave function expands spatially we may find ourselves with insufficient Gaussians to describe properly this expansion. We can however

add a Gaussian by using the reverse procedure: fit the current N-1 Gaussian wave function having the parameters $(\lambda')_A$ to a sum of N new Gaussians, by adjusting the paramters $(\lambda)_A$ to minimize δ. We know that addition of more Gaussians is needed when the eigenvalues of the overlap matrix are all close to one.

This procedure is useful, but unfortunately requires a programmer's supervision and interaction in the course of propagation; one cannot do research and play tennis simultaneously, and this can only diminish the popularity of the method.

VI.4 The use of frozen Gaussians

We should mention that many of these difficulties are eased by the use of Gaussian wave functions with fixed widths which Heller calls frozen Gaussians. Since the width is not changing, the P-Z transform is not required. Empirically we also find that the numerical stability of the MEM equation with frozen Gaussians is greater. At this time our opinion is that more complex problems will be attacked more successfully by using frozen Gaussians. The lack of flexibility caused by the use of a fixed width can be compensated by increasing the number of Gaussians (without necessarily increasing the number of equations).

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APPENDIX A

The Propagation of multiple Gaussian wave functions.

In this Appendix we derive a set of equations frequently used in the text. They give the MEM propagation equations for the case when the wave function is expressed as a sum of Gaussians:

$$\psi(x;t) \equiv \sum_A G_A(x;\{\alpha_A(t),\ \gamma_A(t)\},\{R_A(t),P_A(t)\}) \qquad (A.1)$$

with

$$G_A(x;\{\alpha_A(t),\ \gamma_A(t)\}\ ,\{R_A(t),\ P_A(t)\}) =$$

$$\exp\{(i/\hbar)[\alpha_A(x-R_A(t))^2 + P_A(x-R_A(t)) + \gamma_A]\} \quad . \qquad (A.2)$$

If we compare with the general equation of section II.3.A we have $\Lambda_{A1} = \alpha_A$, $\Lambda_{A2} = \gamma_A$, $\Gamma_{A1} = R_A$, $\Gamma_{A2} = P_A$.

In order to obtain equations for $\dot{\alpha}_A$, $\dot{\gamma}_A$, $\dot{R}_A$ and $\dot{P}_A$ for all the Gaussians we use the equations (II.25). The calculations are lengthy but straightforward. The results are listed below.

For $B\beta$ (in Eq. II.25.a) corresponding to the width parameter α_B of the Gaussian B we have:

$$\sum_A \{<(x - R_B)^2\ G_B|(x-R_A)^2 G_A>(\dot{\alpha}_A + 2\alpha_A^2/m)$$

$$+<(x-R_B)^2 G_B|G_A>(\dot{\gamma}_A - P_A\dot{R}_A - i\hbar\alpha_A/m + P_A^2/2m)$$

$$+<(x-R_B)^2 G_B|(x-R_A)G_A>\ [2\alpha_A(P_A/m - \dot{R}_A) + \dot{P}_A]$$

$$+ <(x-R_B)^2 G_B|\ V\ G_A>\} = 0 \quad . \qquad (A.3)$$

If $B\beta$ (in Eq. II.25.a) corresponds to the parameter γ_B of

the Gaussian B we have:

$$\sum_A \{\langle G_B|(x-R_A)^2\ G_A\rangle\ (\dot{\alpha}_A + 2\alpha_A^2/m)$$

$$+ \langle G_B|G_A\rangle\ (\dot{\gamma}_A - P_A\dot{R}_A - i\hbar\alpha_A/m + P_A^2/2m)$$

$$+ \langle G_B|(x-R_A)\ G_A\rangle[2\alpha_A(P_A/m - \dot{R}_A) + \dot{P}_A]$$

$$+ \langle G_B|V\ G_A\rangle\} = 0 \quad . \qquad (A.4)$$

If Bb in Eq. (II.25.b) is the parameter P_B of the Gaussian B we obtain

$$\mathrm{Re}\ \Omega = 0 \qquad (A.5)$$

with

$$\Omega \equiv \sum_A (\langle (x-R_B)\ G_B\ |(x-R_A)^2 G_A\rangle\ (\dot{\alpha}_A + 2\alpha_A^2/m)$$

$$+ \langle (x-R_B)G_B|G_A\rangle(\dot{\gamma}_A - P_A\dot{R}_A - i\hbar\alpha_A/m + P_A^2/2m)$$

$$+ \langle (x-R_B)G_B|(x-R_A)G_A\rangle[2\alpha_A(P_A/m - \dot{R}_A) + \dot{P}_A]$$

$$+ \langle (x-R_B)G_B|VG_A\rangle\} = 0 \qquad (A.6)$$

Finally if Bb in Eq. (II.25.b) is the parameter R_B of the Gaussian B we obtain

$$\mathrm{Im}\ \Omega = 0 \quad . \qquad (A.7)$$

The physical significance of these equations, the method of solving them and various approximations are discussed in the text.

For a variety of reasons, specified in various places in the paper it is useful to rewrite the equations of motion for the

trajectories in a different form. To do this we use the notation

$$M(An|Bm) \equiv \int dx (x-R_A)^n \, G_A^* \, (x-R_B)^m \, G_B \qquad (A.8)$$

$$V(An|Bm) = \int dx (x-R_A)^n G_A^*(x) \; V(x) (x-R_B)^m G_B(x) \qquad (A.9)$$

We can then summarize the equations (A3-A7) as

$$\overleftrightarrow{M} \cdot \vec{X} = \vec{v} \qquad (A.10)$$

where

$$\vec{X} \equiv \begin{pmatrix} P_A^2/2m - P_A\dot{R}_A - i\hbar\alpha_A/m + \dot{\gamma}_A \\ P_B^2/2m - P_B\dot{R}_B - i\hbar\alpha_B/m + \dot{\gamma}_B \\ 2\alpha_A(P_A/m - \dot{R}_A) + \dot{P}_A \\ 2\alpha_B(P_B/m - \dot{R}_B) + \dot{P}_B \\ \dot{\alpha}_A + 2\alpha_A^2/m \\ \dot{\alpha}_B + 2\alpha_B^2/m \end{pmatrix} \equiv \begin{pmatrix} X_1 \\ X_2 \\ X_3 \\ X_4 \\ X_5 \\ X_6 \end{pmatrix} \qquad (A.11)$$

$$\overleftrightarrow{M} \equiv \begin{pmatrix} M(A0|A0) & M(A0|B0) & 0 & M(A0|B1) & M(A0|A2) & M(A0|B2) \\ M(B0|A0) & M(B0|B0) & M(B0|A1) & 0 & M(B0|A2) & M(B0|B2) \\ 0 & M(A1|B0) & M(A1|A1) & M(A1|B1) & 0 & M(A1|B2) \\ M(B1|A0) & 0 & M(B1|A1) & M(B1|B1) & M(B1|A2) & 0 \\ M(A2|A0) & M(A2|B0) & 0 & M(A2|B1) & M(A2|A2) & M(A2|B2) \\ M(B2|A0) & M(B2|B0) & M(B2|A1) & 0 & M(B2|A2) & M(B2|B2) \end{pmatrix} \qquad (A.12)$$

$$\vec{v} \equiv - \begin{pmatrix} V(A0|A0) + V(A0|B0) \\ V(B0|A0) + V(B0|B0) \\ V(A1|A0) + V(A1|B0) \\ V(B1|A0) + V(B1|B0) \\ V(A2|A0) + V(A2|B0) \\ V(B2|A0) + V(B2|B0) \end{pmatrix} \equiv \begin{pmatrix} V_1 \\ V_2 \\ V_3 \\ V_4 \\ V_5 \\ V_6 \end{pmatrix} \qquad (A.13)$$

Another useful form is .

$$\overleftrightarrow{M} \cdot \vec{\underset{\sim}{X}} = \vec{\underset{\sim}{v}}$$

with

$$\vec{\underset{\sim}{X}} = \begin{pmatrix} X_1 + V(R_A) \\ X_2 + V(R_B) \\ X_3 + \partial V(R_A)/\partial R_A \\ X_4 + \partial V(R_B)/\partial R_B \\ X_5 + (1/2)\partial^2 V/\partial R_A^2 \\ X_6 + (1/2)\partial^2 V/\partial R_B^2 \end{pmatrix} \qquad (A.14)$$

and $\vec{\underset{\sim}{v}}$ is obtained from $\vec{v}$ by replacing V(An|Bm) with

$$\underset{\sim}{V}(An|Bm) = \int dx\{(x-R_A)^n \, G_A^*(x)[V(x) - V(R_B) - -(\partial V(R_B)/\partial R_B)(x-R_B) - (1/2)(\partial^2 V(R_B)/\partial R_B^2)(x-R_B)^2] \cdot (x-R_B)^m \, G_B(x)\}$$

Thus SHM is obtained by taking $\vec{\underset{\sim}{v}} = 0$.

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Figure Captions

Figure 1. The "length", defined as $l(t) = (\hbar/2\mathrm{Im}\alpha(t))^{1/2}$, of a normalized, initially narrow, low energy Gaussian wave packet propagated in a Morse potential (Eq. (III.12a)) using the MEM equations (Eq. (III.5)) (———). $l(t)$ is in units of λ^{-1} and time is in units of $\tau = (2m/D)^{1/2}\,\pi\,\lambda^{-1}$, where $\lambda = 1.846\ \text{Å}^{-1}$ and $D = 4.334$ a.m.u. $\text{Å}^2/10^{-28}$ sec^2 are the Morse potential range parameter and well depth, respectively, and $m = 0.5$ a.m.u. is the reduced mass of the oscillator. For values of l higher than .22, the LHA equation for the force is in error by more than 10%. Initial values of the wave packet parameters are: $\mathrm{Re}(\alpha) = 0.0$ a.m.u./10^{-14} sec; $\mathrm{Im}(\alpha) = 8.0$ a.m.u./10^{-14} sec; $P = 0.0$ a.m.u. Å/10^{-14} sec; $R = 0.20$ Å; $\mathrm{Re}(\gamma) = 0.1878$ a.m.u. $\text{Å}^2/10^{-14}$ sec; and $\mathrm{Im}(\gamma) = -0.0696$ a.m.u. $\text{Å}^2/10^{-14}$ sec.

Figure 2. The force (in units of $D\lambda$) exerted on the center of the wave packet whose parameters are defined in Fig. 1, propagated using the MEM equations (III.5b) (———) and the LHA equations (III.7b). (-- —— --).

Figure 3. The Morse potential averaged over Gaussians of different width, $\langle G\,V\,G\rangle/\langle G\,G\rangle$ (in units of D), as a function of R (in units of λ^{-1}) using $l = 0.60$ (-- —— --), $l = 0.329$ (·———·), and $l = 0.147$ (---); we also plot the Morse potential $V(R)$ (———).

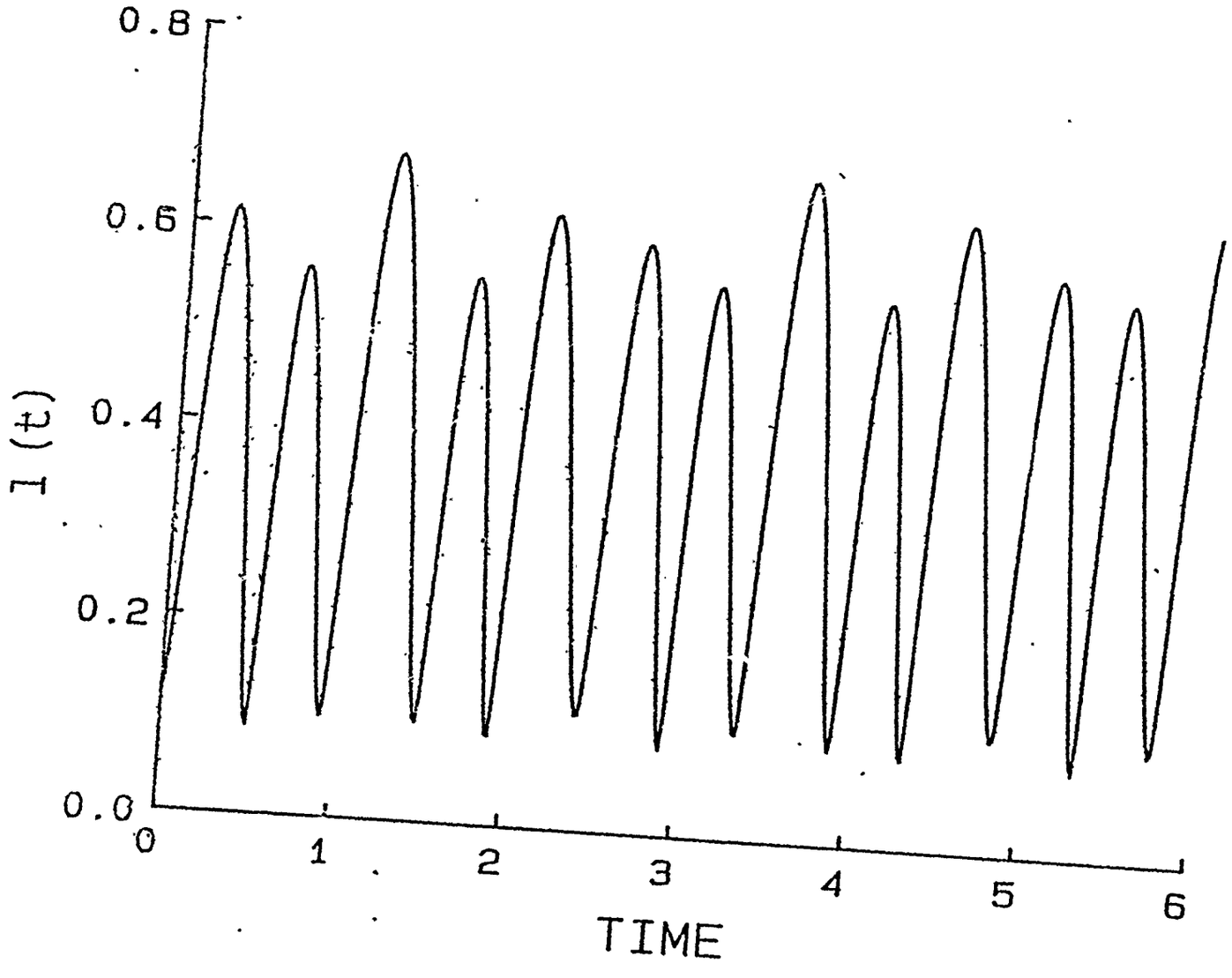
Figure 4. The potential energy $V(R(t))$ (in units of D) as a function of time for the wave packet of Fig. 1 propagated using the MEM equations (———) and the LHA equations (-- —— --).

Figure 5. The quantum energy, $\langle G|H|G\rangle$ (in units of $\dot{D}$), as a function of time for the wave packet of Fig. 1 propagated using the MEM equations (——) and the LHA equations (-- —— --).

Figure 6. The "classical energy," $\langle G|V|G\rangle + P^2/2m$ (for MEM) or $V(R) + P^2/2m$ (for LHA), as a function of time, for the wave packet of Fig. 1. propagated using the MEM equations (——) and the LHA equations (-- —— --).

Figure 7. The real part of the Fourier transform of $\langle\psi(x;t)|\psi(x;t_o)\rangle$, Eq. (V.2), where the initial wave function $\psi(x;t_o) = 0.5\ (\phi_o(x) + \phi_1(x) + \phi_2(x) + \phi_3(x))$ is represented by four wave packets, $\phi_n(x)$ are the Morse eigenstates, and $\psi(x;t)$ is propagated using the MEM equations (——), and the uncoupled IGA equations (-- —— --). The peaks of $\mathrm{Re}C(\omega)$ are related to the probability of being in eigenstate $\phi_n(x)$ by Eq. (V.3). In this plot $T = 5.0$, $\lambda = 1.06$.

Figure 8. The square of the projection of the wave function (Eq. III.25) propagated by IGA onto the Morse eigenstates, i.e., $|\langle\phi_n|\psi(t)\rangle|^2$, versus time for n = 0 (——), n=1 (--), n=2 (- · -) and n=3 (-- —— --).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0.6
0.4
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I (t)
0
1
2
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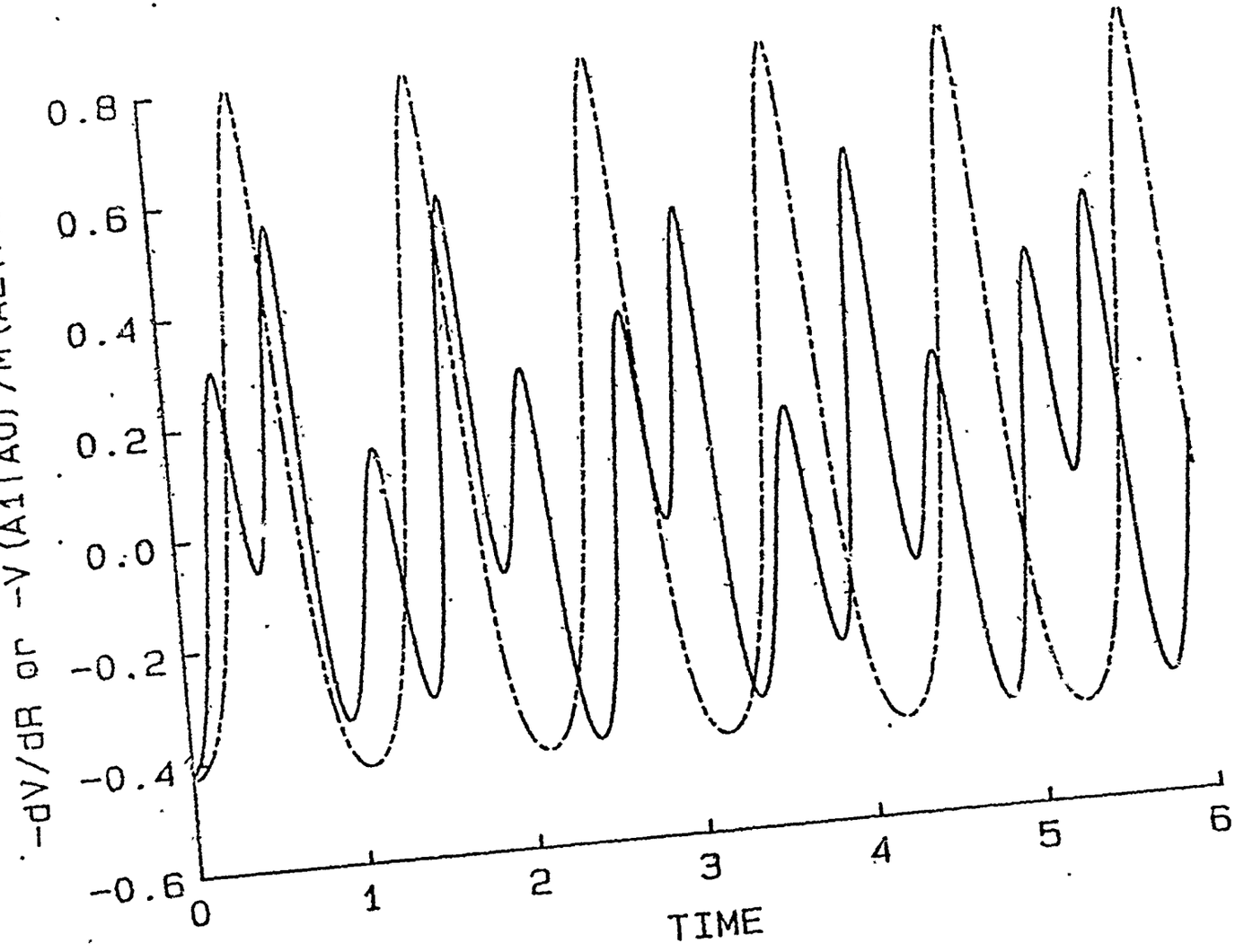
TIME


0.8
0.6
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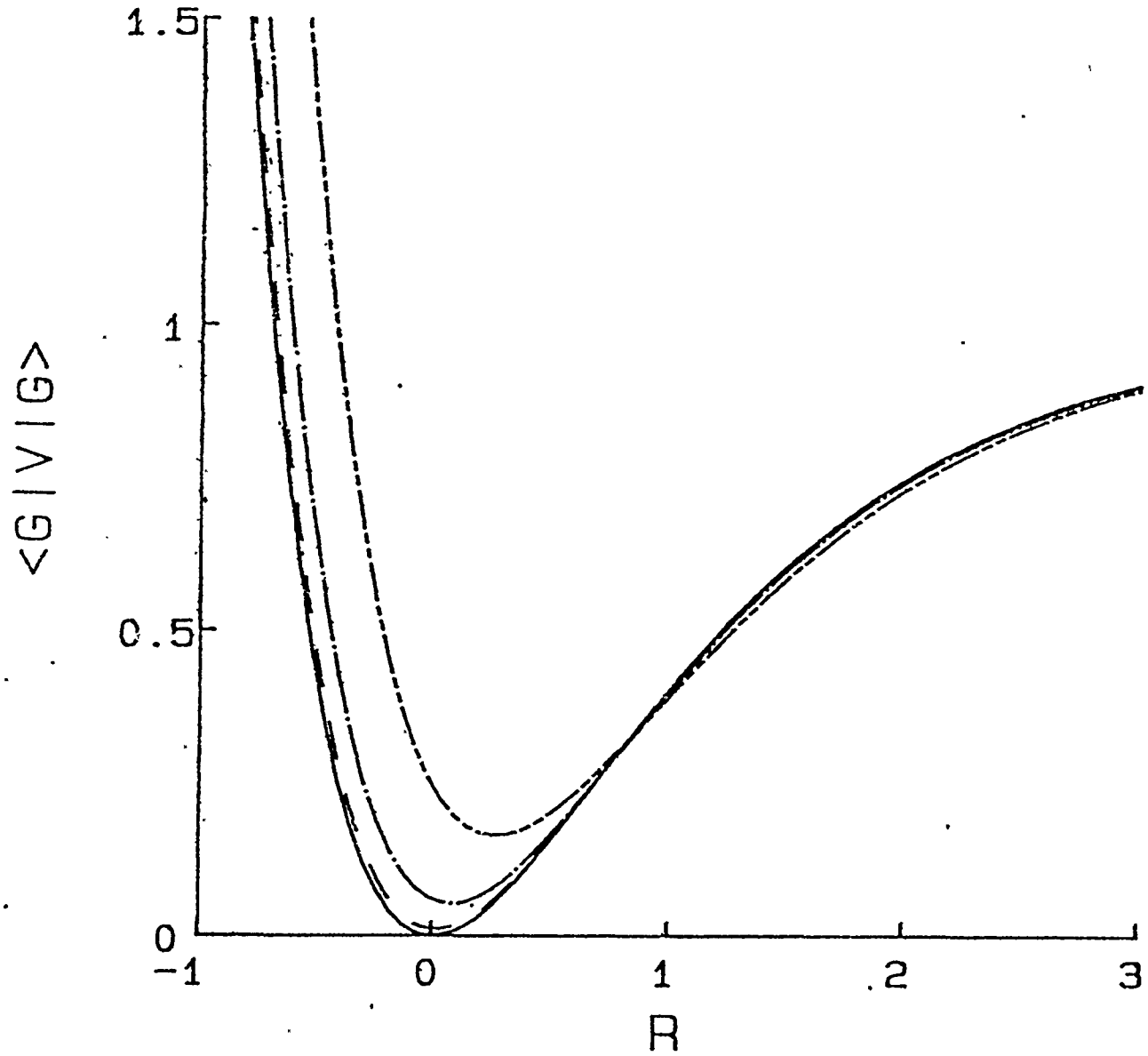
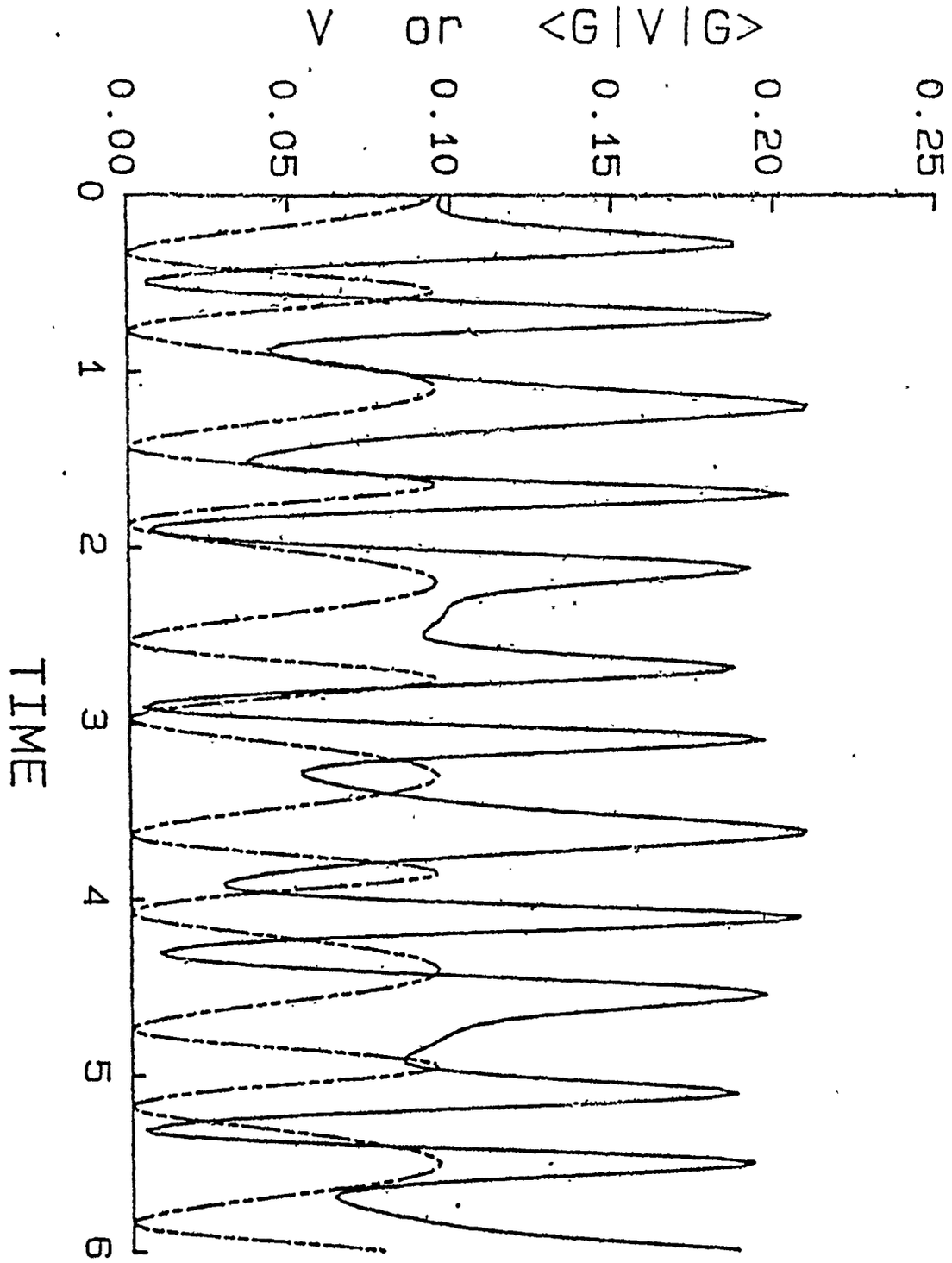
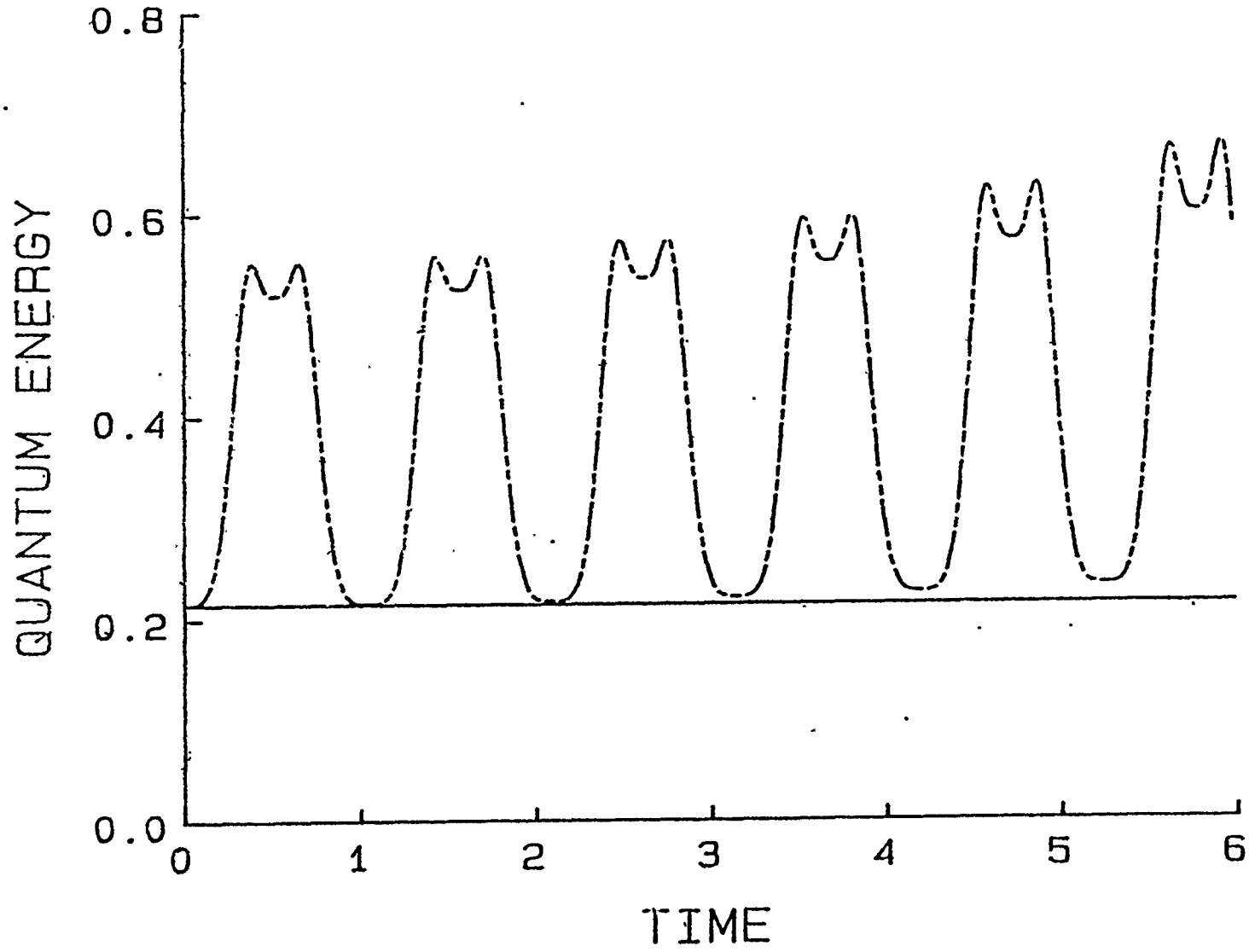
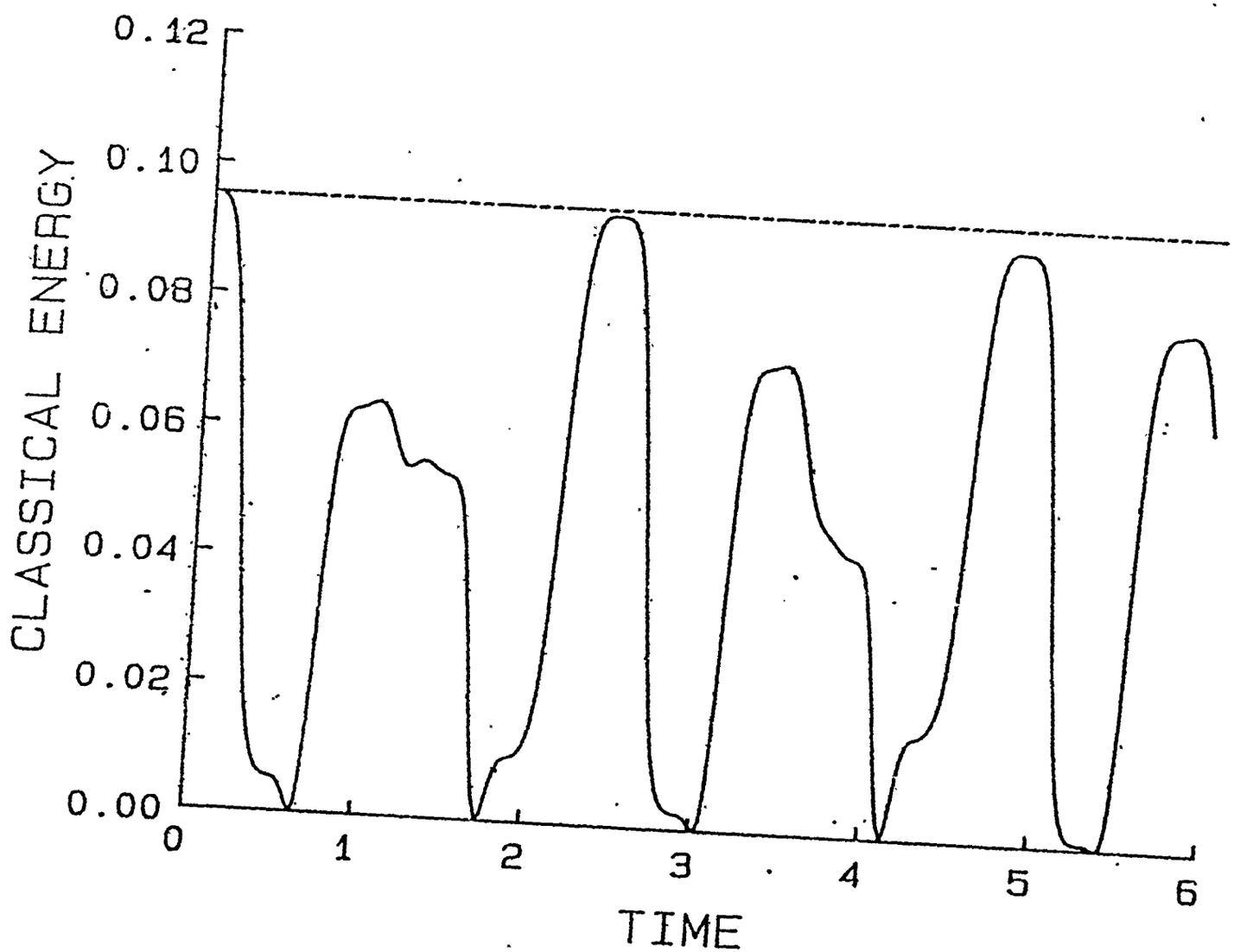
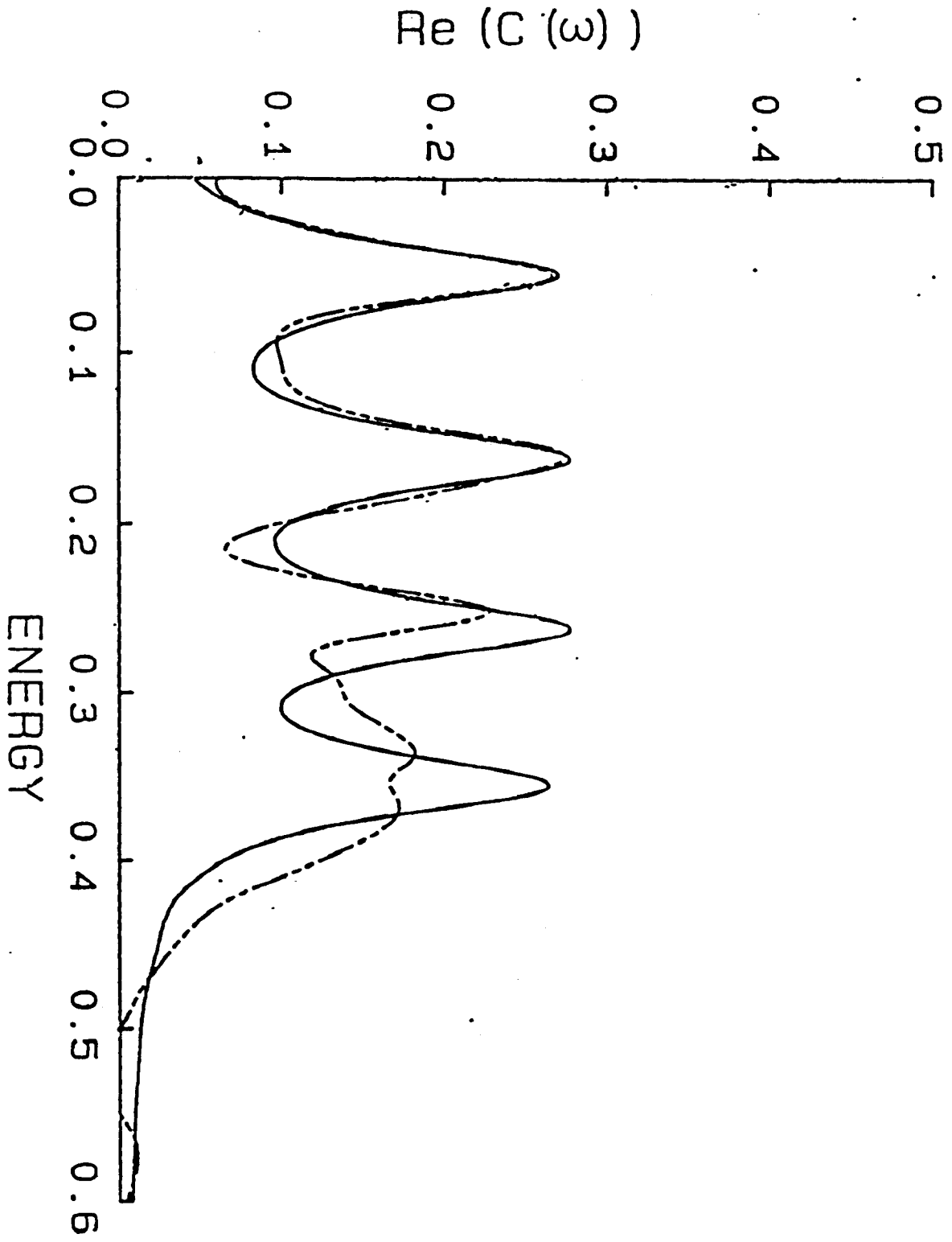
-0.4
-0.6
-dV/dR or -V(A1|A0)/M(A2|A0)
0
1
2
3
4
5
6
TIME

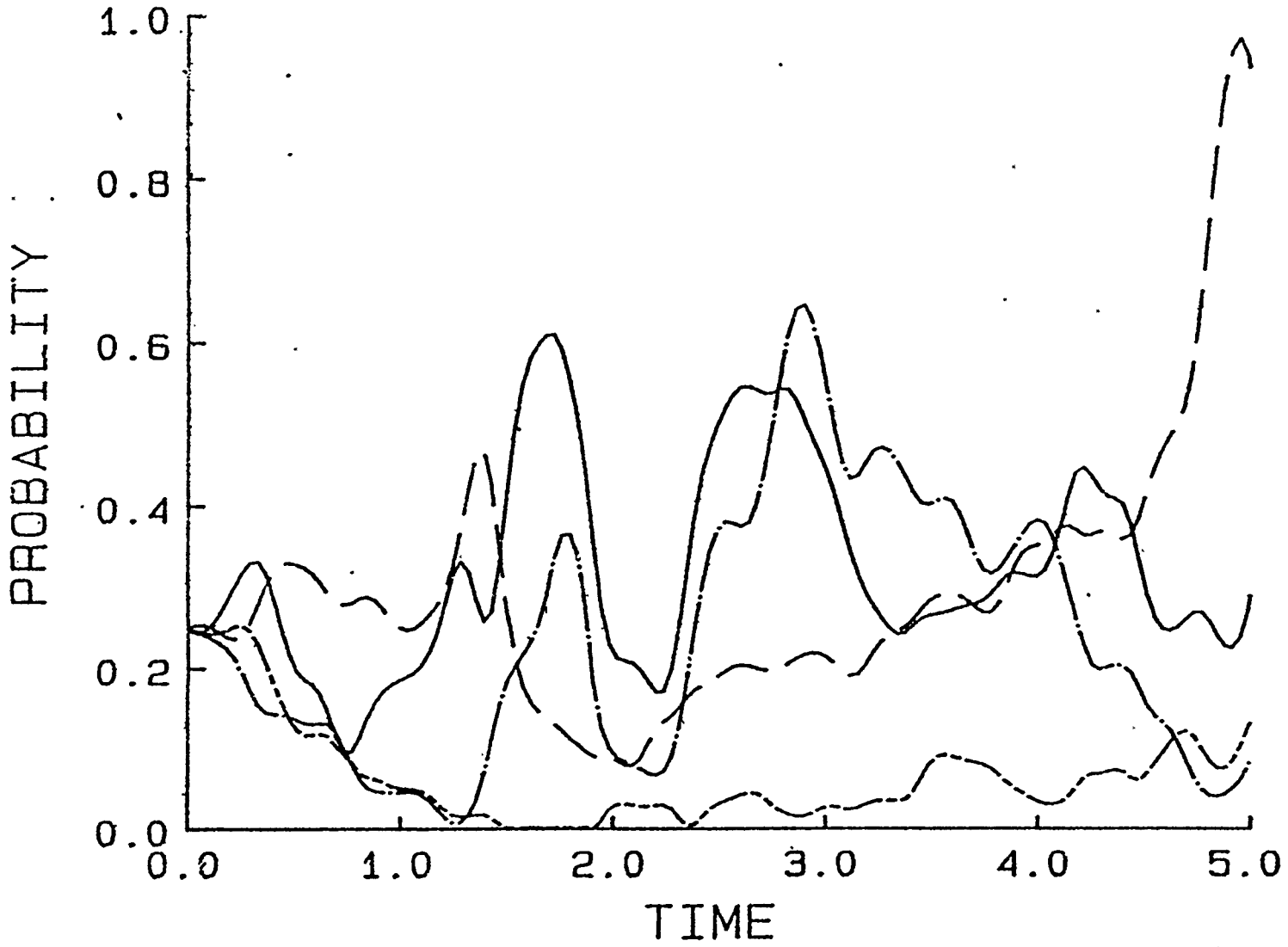

1.5
1
0.5
0
<G|V|G>
-1
0
1
.2
3
R


V or <G|V|G>
0.00
0.05
0.10
0.15
0.20
0.25
0
1
2
3
4
5
6
TIME


QUANTUM ENERGY
0.8
0.6
0.4
0.2
0.0
0
1
2
3
4
5
6
TIME


0.12
0.10
0.08
0.06
0.04
0.02
0.00
CLASSICAL ENERGY
0
1
2
3
4
5
6
TIME


Re (C (ω))
0.0
0.1
0.2
0.3
0.4
0.5
ENERGY
0.0
0.1
0.2
0.3
0.4
0.5
0.6


1.0
0.8
0.6
0.4
0.2
0.0
PROBABILITY
0.0
1.0
2.0
3.0
4.0
5.0
TIME